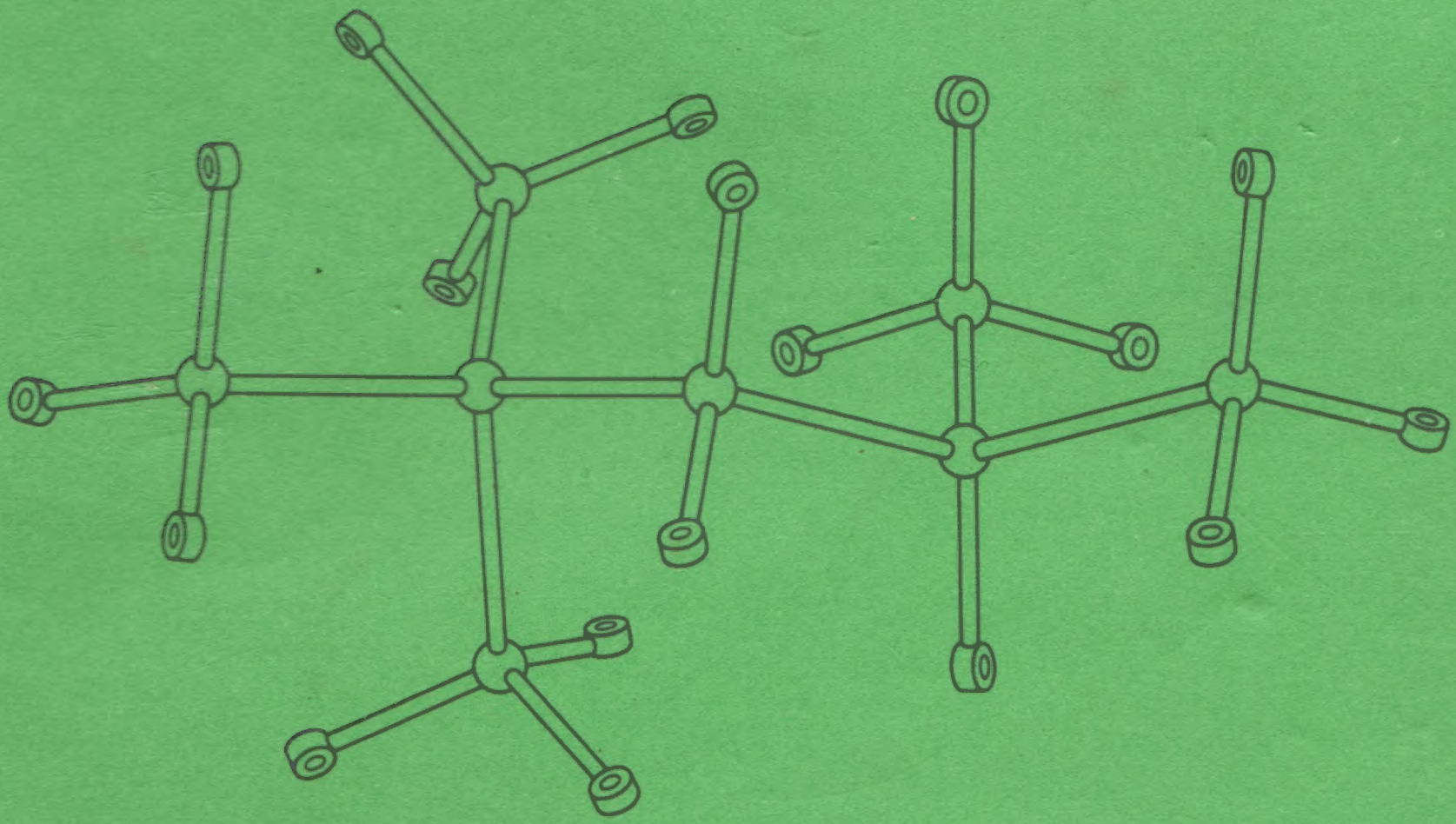
Minit and Orbit molecular building systems



Organic and inorganic chemistry

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Organic and inorganic chemistry

Instructions and notes on the use of the Minit and Orbit molecular building systems by **R S Lowrie** MA, D Phil, FRIC

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Introduction

The Minit and Orbit molecular building systems are designed to enable you to build up molecular and crystal structures and hence to solve problems of structure and stereochemistry. The atoms consist of plastic centres having prongs set at the correct bond angles. The centres are colour coded according to the element, and the bond angles are engraved on the centres in the Orbit system, and marked by bars in the Minit system where necessary.

Bonds between atoms are made from plastic straws, which can be cut to any required length. Covalent bonds are normally represented by green straws; white straws can be used for other purposes, such as hydrogen bonds. Multiple bonds may be shown using flexible straws.

In the text the bond lengths for the Minit system are given first, followed by the bond lengths for the Orbit system in brackets. The recommended bond lengths have been simplified and the models in this book can be built quite satisfactorily with tubes of two lengths only, Minit 1.5 and 2.5 cm (Orbit 3.5 and 5.0 cm). Any exceptions are given in the text. For building with greater accuracy students will need to choose a suitable scale say 2 cm = 100 pm (or 1 Å) (Orbit 3 cm = 100 pm) and then calculate their own bond lengths by adding together the covalent radii of the bonding atoms (see table I) and converting these into cm. Finally the straw length to be cut will be 0.6 cm (Orbit 1 cm) less to allow for the radius of the atom centre.

Example in Minit:

Calculation of H—N bond length

Scale	2 cm = 100 pm
Covalent radii	H 30 pm
	N 70 pm
	100 pm

Bond length 2.0 cm. Straw length 2.0—0.6 = 1.4 cm

Example in Orbit:

Calculation of H—N bond length

Scale	3 cm = 100 pm
Covalent radii	H 30 pm
	N 70 pm
	100 pm

Bond length 3 cm. Straw length (3—1) cm = 2 cm

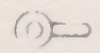
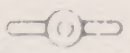
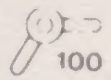
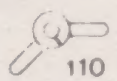
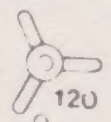
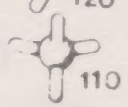
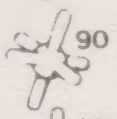
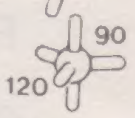
---

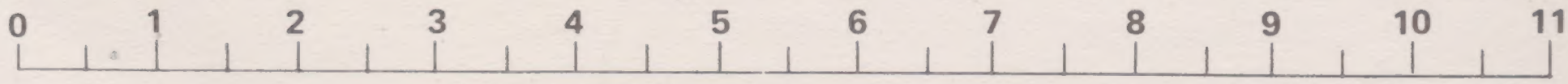
†This is a different scale to that recommended in the biochemistry set, where larger models require a smaller scale.

Table I

Element	*Colour of atom centre*		*Van der Waals radii (pm)*	*Covalent radii*		
				Single bond (pm)	*Double bond (pm)*	*Triple bond (pm)*
Hydrogen	H	White	100	30	–	–
Carbon	C	Black	170	77	67	62
Nitrogen	N	Blue	160	70	62	55
Oxygen	O	Red	140	67	55	–
Phosphorus	P	Purple	190	110	100	–
Sulphur	S	Yellow	185	100	95	–
Metals	M	Silver	various	various	–	–
Halogens	Hal	Green	various	various	–	–
Fluorine	F	Light-green	140	65	–	–
Chlorine	Cl	Green	180	99	–	–
Bromine	Br		195	115	–	–
Iodine	I		215	135	–	–

Table II
Code letters denoting the shapes of atom centres to be found in the set.

Type of atom	*Code letter*	*Number of prongs*	*Bond/prong angles (degrees)*	*Shape of atom model and bond angles*
Univalent	a	1	–	
Diunivalent	b	2	180	
	c	2	100	
	d	2	110	
	j	3	120	
Tetrahedral	k	4	110	
Octahedral	l	6	90	
Trigonal bipyramid	m	5	{ 120 90	



1 Principles of molecular shape

Molecules based upon the tetrahedron

The positions of the bonds from an atom are determined by the fact that the electron pairs forming the bonds repel one another electrostatically. For instance, tetrachloromethane, CCl_4, has four electron-pair bonds C—Cl. If the bonds were arranged in a square planar fashion, there would be a 90° angle between adjacent bonds. Construct a model of the molecule CCl_4, using a black carbon centre, C^k, and four green chlorine centres, Cl^a, linked by 2.5 cm (Orbit 5.0 cm) green straws. Now thread a length of cotton through the chlorine centres so that all the chlorine atoms are joined to one another, as in figure 1. Note that the shape formed is a triangular pyramid, or *tetrahedron.*

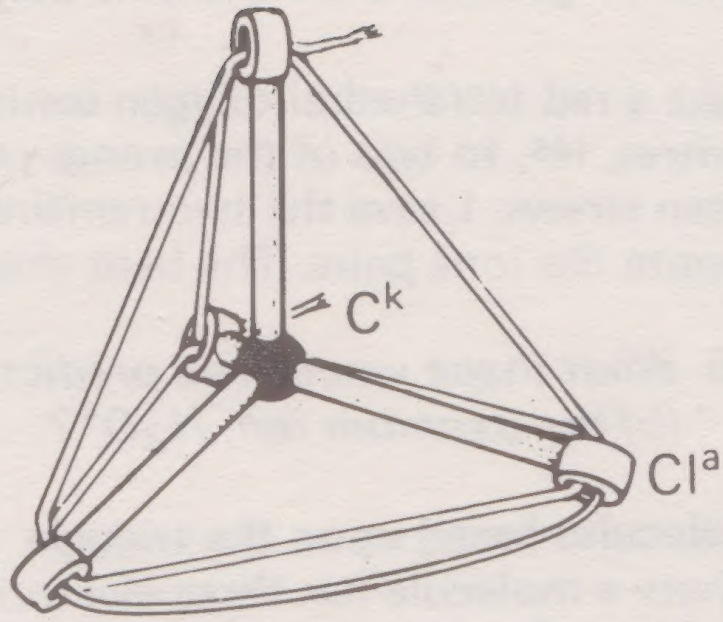


Figure 1
Tetrachloromethane, with cotton

1.1 *What is the angle between adjacent bonds? Measure the angles with a protractor, and check that they are all approximately equal.*

1.2 *Is it possible to devise a shape for CCl_4 in which all the bond angles are greater than this?*

The four chlorine atoms are at the corners of a tetrahedron with the carbon atom at its centre.

Ammonia, NH_3, contains three electron-pair bonds, N—H, and one lone pair (figure 2).

The shape of the ammonia molecule is the result of the four electron pairs (three bond pairs and one lone pair) repelling each other. To construct a model, take a blue tetrahedral nitrogen centre, N^k, and attach hydrogen centres, H^a, to three of the prongs using 1.5 cm (Orbit 3.5 cm) green straws. Leave the fourth prong unoccupied to depict the lone pair.

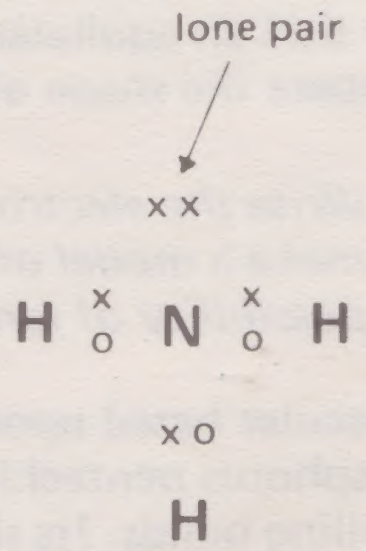


Figure 2 Ammonia

1.3 *Describe the shape of the ammonia molecule.*

1.4 *What shape would you predict for the ammonium ion, NH_4^+?*

Water, H_2O, has the electronic configuration shown in figure 3.

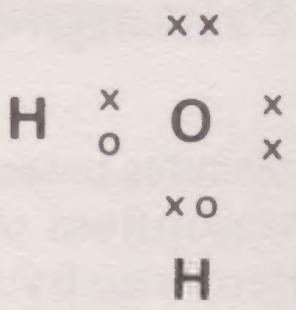


Figure 3 Water

Take a red tetrahedral oxygen centre, O^k, and attach hydrogen centres, H^a, to two of the prongs using 1.5 cm (Orbit 3.5 cm) green straws. Leave the two remaining prongs vacant to denote the lone pairs. The bent shape is readily seen.

1.5 *What shape would you predict for (a) H_2S; (b) the oxonium ion, H_3O^+?*

Molecules based upon the triangle

Where a molecule has three electron-pair bonds and no lone pairs, the shape is planar instead of pyramidal. The planar shape allows the angle between bonds to be 120° ie the separation is greater than in NH_3. Boron trichloride, BCl_3, is one example. The 6-ring planar carbon centre, C^i, can be used to represent boron in this example. Simply join three chlorine centres, Cl^a, to it using 2.5 cm (Orbit 5.0 cm) green straws. Thread a length of cotton through the chlorine centres and note that an equilateral triangle results (figure 4). Compare the shape of this molecule with that of NH_3.

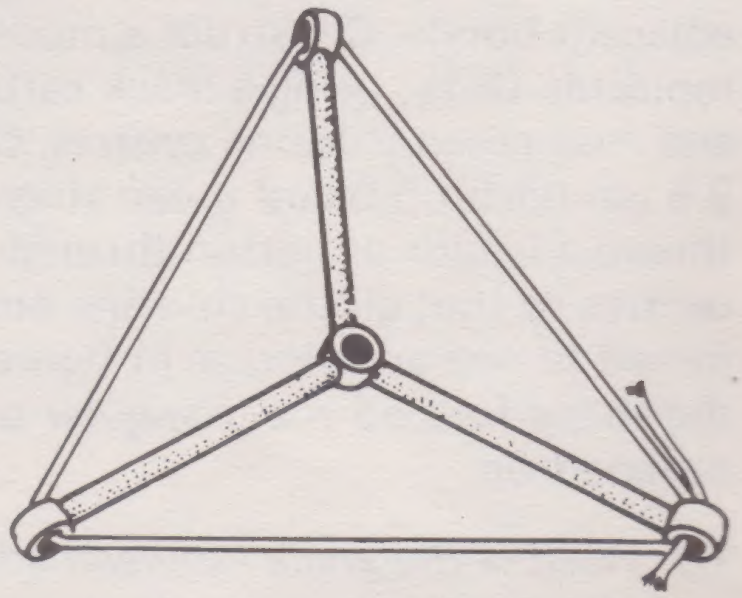


Figure 4 Boron trichloride, with cotton

1.6 *Write the electronic configuration of PCl_3, and make a model of it, taking into account the possibility of lone pair formation.*

Molecules based upon the trigonal bipyramid

Phosphorus pentachloride, PCl_5, has five repelling bonds. Its shape may be derived from that of BCl_3 by adding a 7 cm (Orbit 10 cm)

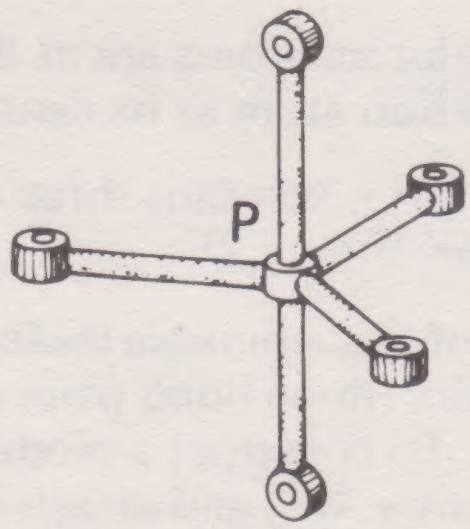


Figure 5 Phosphorus pentachloride

length of green straw through the centre atom, as shown in figure 5, and adding a chlorine centre, Cl^a, at the end of each axial bond so formed.

The kit provides a five-pronged phosphorus centre, P^m. Take one such centre, add five 2.5 cm (Orbit 5.0 cm) straws and five chlorine centres, Cl^a. To enable the shape to be seen more clearly, take a length of cotton and thread it through the chlorine centres, as shown in figure 6. The shape is that of two pyramids base-to-base, ie: a *trigonal bipyramid.*

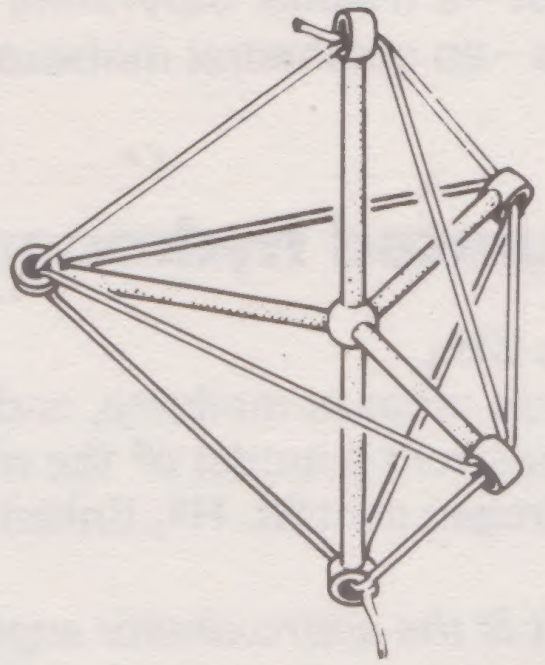


Figure 6 Phosphorus pentachloride, with cotton

1.7 *Write electronic configurations for SF_4 and ClF_3, and attempt to predict their shapes. Will the shapes be based upon the trigonal bipyramid?*

Molecules based upon the octahedron

Sulphur hexafluoride, SF_6, has six repelling bonds directed to the corners of an octahedron. Take the sulphur octahedral centre and attach six F^a centres to it using 2.5 cm (Orbit 5.0 cm) green straws. Thread a length of cotton through the chlorine centres as before and observe the octahedron produced.

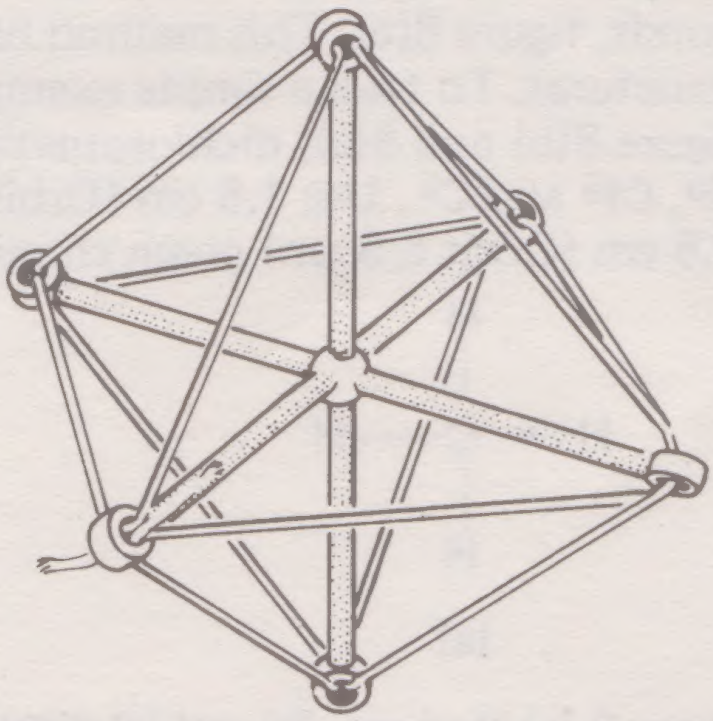


Figure 7 Sulphur hexafluoride, with cotton

1.8 *Measure the angles between adjacent bonds.*

1.9 *Write the electronic structure, and hence predict the shape of BrF_5.*

Summary

The shape of simple molecules are determined by the number of bonds plus the number of lone pairs in the valence shell of the centre atom.

Three bonds—a triangular molecule
Four bonds—a tetrahedral molecule

Three bonds plus one lone pair—a pyramidal molecule
Two bonds plus two lone pairs—a bent molecule
Five bonds—a trigonal bipyramid
Six bonds—an octahedral molecule

2 Saturated hydrocarbons

Methane, CH_4

The carbon atom in methane, and in all 'saturated' structures, is tetrahedral in configuration. Construct a model of the molecule CH_4 using a tetrahedral carbon centre, C^k, and four hydrogen centres, H^a, linked by 1.5 cm (Orbit 3.5 cm) green straws.

2.1 *What is the approximate angle between adjacent bonds? Measure the angles with a protractor, and check that they are all the same.*

It is difficult to represent three-dimensional structures on paper, and it is conventional to show the bonds as if they lie in a plane, with an angle of 90° between adjacent bonds, figure 8(a). This method has limitations when depicting more complicated structures. To take a simple example, construct models of the structures shown in figure 8(b) and 8(c), dichloromethane, CH_2Cl_2. You will need the following centres: H^a, Cl^a and C^k. Use 1.5 cm (Orbit 3.5 cm) green straws to depict C–H bonds, and 2.5 cm (Orbit 5.0 cm) green straws to depict C–Cl bonds.

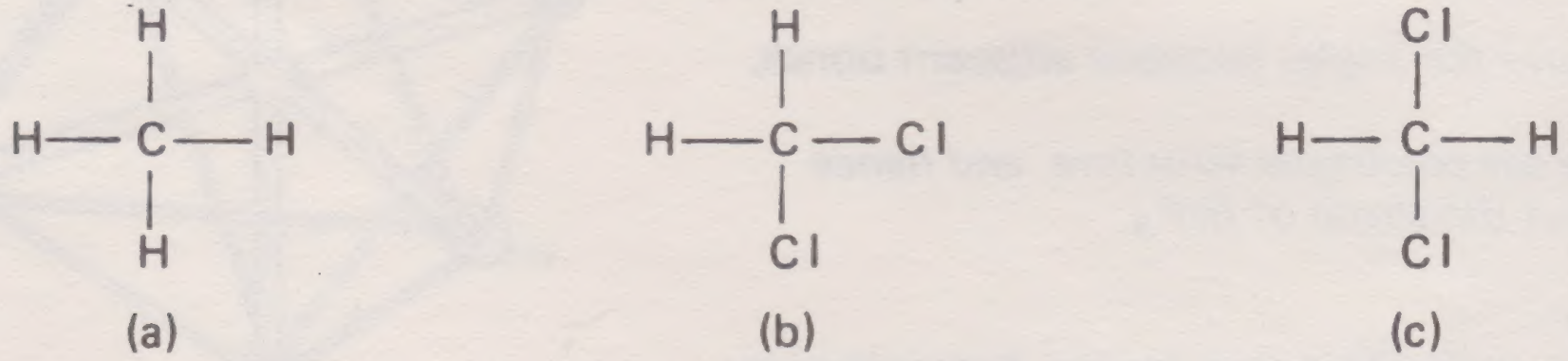


Figure 8 (a) Methane, (b) and (c) dichloromethane

2.2 *Do structures (b) and (c) represent the same or different molecules? If you are in any doubt, rotate both models in such a way as to try to make them coincide.*

Ethane, C_2H_6 and propane, C_3H_8

Construct a model of the molecule ethane, C_2H_6, using two tetrahedral carbon centres, C^k, and six hydrogen centres, H^a, as in figure 9(a). Use 1.5 cm (Orbit 3.5 cm) straws for C–H bonds, and a 2.5 cm (Orbit 5.0 cm) straw for the C–C bond. Notice that the straws allow free rotation, so that the methyl groups CH_3 can be rotated relative to one another. Free rotation is typical of single-bond links.

Now construct a model of 1,2- dichloroethane, $C_2H_4Cl_2$, figure 9(b). Use 3.5 cm (Orbit 5.0 cm) green straws for the C–Cl bonds. Since the end groups can be rotated relative to one another, it is not possible to make more than one kind of molecule with the two chlorine atoms attached to different carbon atoms.

2.3 *Construct a model of 1,1-dichloroethane, figure 9(c). How many different kinds of molecule (isomers) are there corresponding to the molecular formula $C_2H_4Cl_2$?*

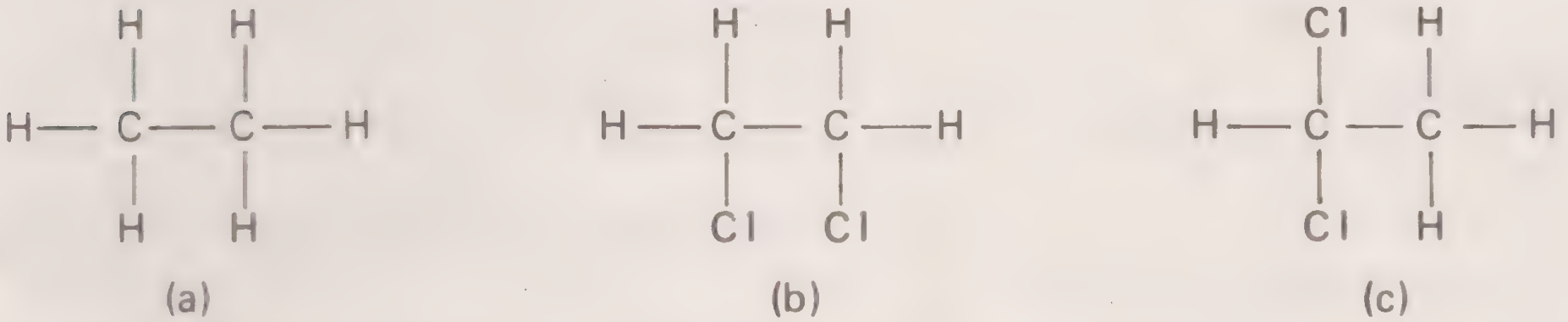
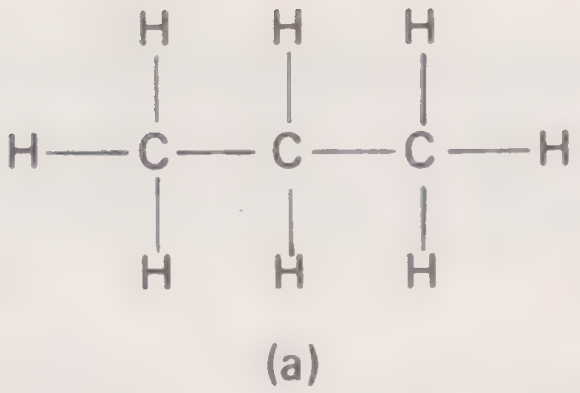


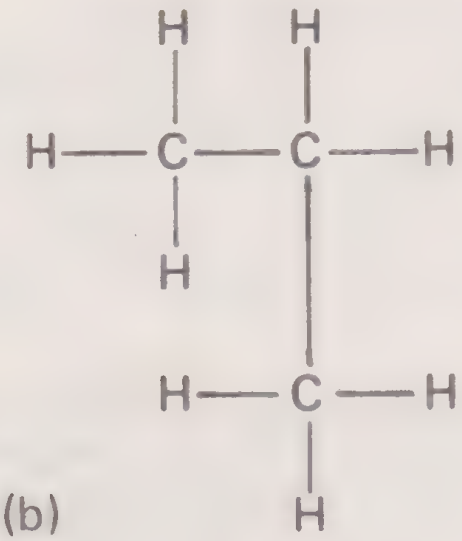
Figure 9 (a) Ethane (b) 1,2-dichloroethane (c) 1,1-dichloroethane

Now construct the two structures C_3H_8 depicted in figure 10 using straw lengths as above. You have made molecules of the next alkane hydrocarbon, propane. Experiment with rotating the carbon-carbon bonds in the same way as you did with ethane structures.

2.4 *How many different structures can you make, corresponding to C_3H_8, allowing for the fact that if one shape can be converted into another by free rotation, the substances represented are in fact the same.*



(a)



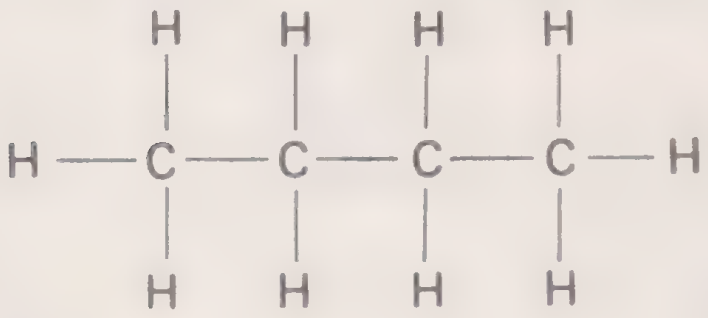
(b)

Figure 10 Two alternative representations of propane

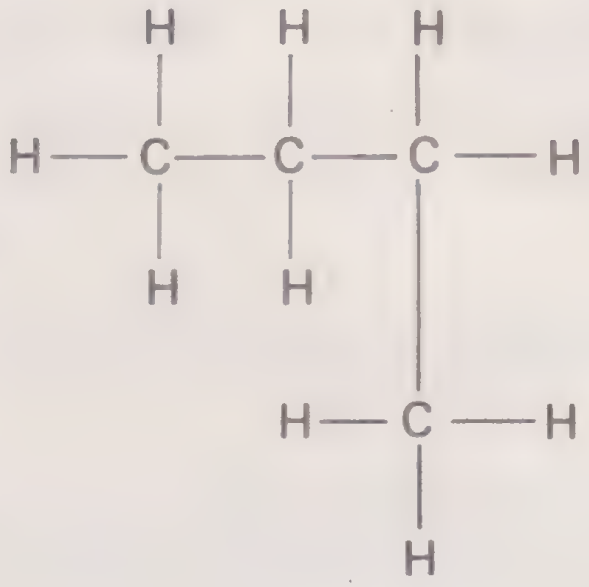
2.5 *Try to work out on paper how many isomers of chloropropane C_3H_7Cl, can be made. Verify your predictions by constructing models.*

2.6 *How many isomers of dichloropropane, $C_3H_6Cl_2$, are there?*

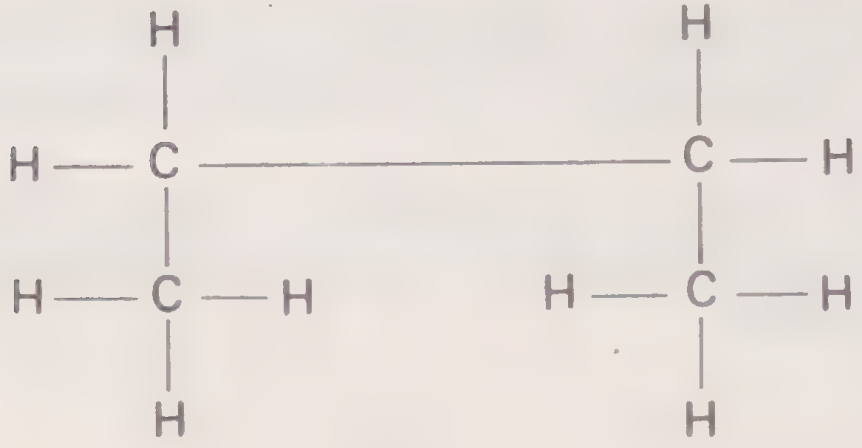
Butane, C_4H_{10}



(a)



(b)



(c)

Figure 11 Butane—three alternative representations

2.7 *Examine the three different diagrams in figure 11. Do they in fact represent different molecules, allowing for free rotation of groups about the carbon-carbon bonds?*

The three diagrams in figure 11 all contain a so-called 'straight-chain' of carbon atoms. This is usually depicted on paper as C—C—C—C although if the atoms are not printed in a straight line it does not matter. There is only one straight chain isomer of butane, often called normal-butane or *n*-butane. The carbon 'backbone' is in fact not straight but zig-zag, as your model should show. In a solid crystal, a regular zig-zag is formed, but in the liquid and vapour phases, rotation can occur about all the bonds, and the backbone can twist into all sorts of shapes without the structure breaking up.

Construct another model of C_4H_{10}, this time using the 'branched chain' configuration shown in figure 12. This represents an isomer of normal butane, sometimes referred to as iso-butane, although a better name is methylpropane.

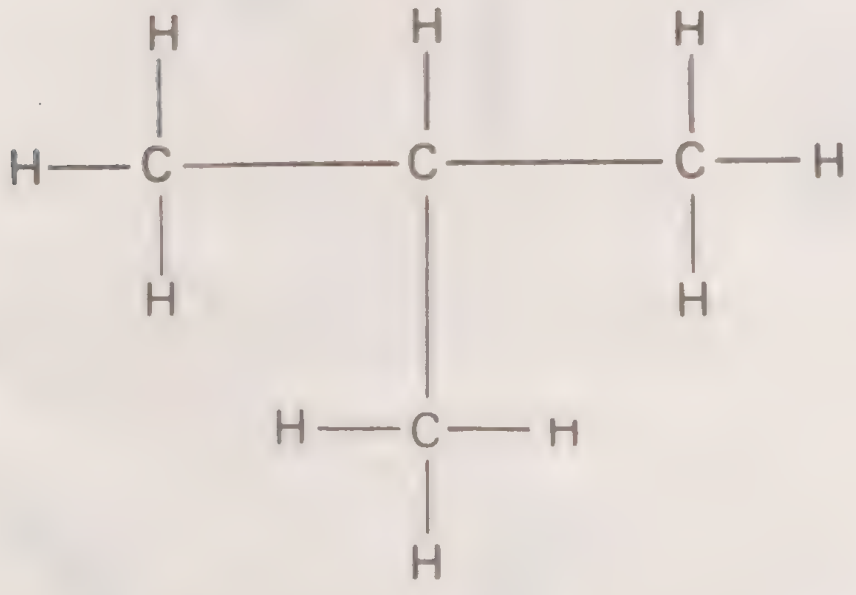


Figure 12 Methylpropane

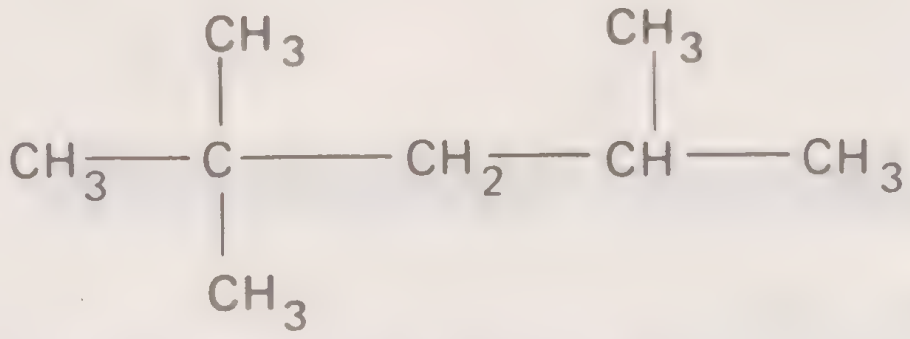


Figure 13 2,2,4-Trimethylpentane

2.8 *Are there any other possible isomers of molecular formula C_4H_{10}?*

Higher alkanes

Crude petroleum consists essentially of a mixture of alkanes with varying numbers of carbon atoms up to about 30. Most naturally occurring alkanes are 'straight-chain', but

branched-chain alkanes are important commercially. For instance, 2,2,4-trimethylpentane is an important constituent of motor fuel.

Construct a model of 2,2,4-trimethylpentane.

2.9 *How many isomers do you think there are for 2,2,4-trimethylpentane?*

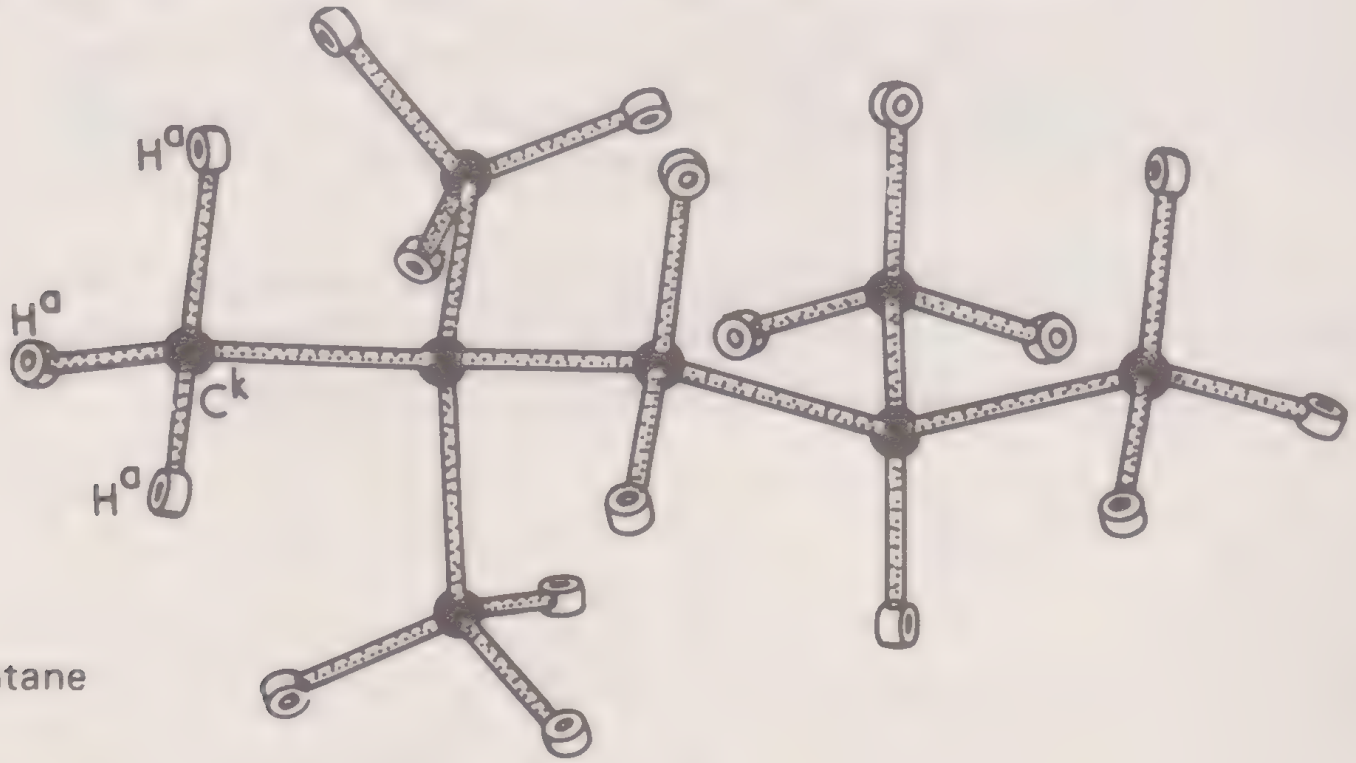


Figure 14 2,2,4-Trimethylpentane

3 Unsaturated hydrocarbons

Ethene, C_2H_4

Take two tetrahedral carbon centres, C^k, and join two hydrogen centres H^a to each using 1.5 cm (Orbit 3.5 cm) green straws. Now take two 2.5 cm (Orbit 5 cm) flexible straws and make a double bond linkage between the carbon centres, (figure 15). Each flexible straw represents an electron pair, in the same way as rigid straws do.

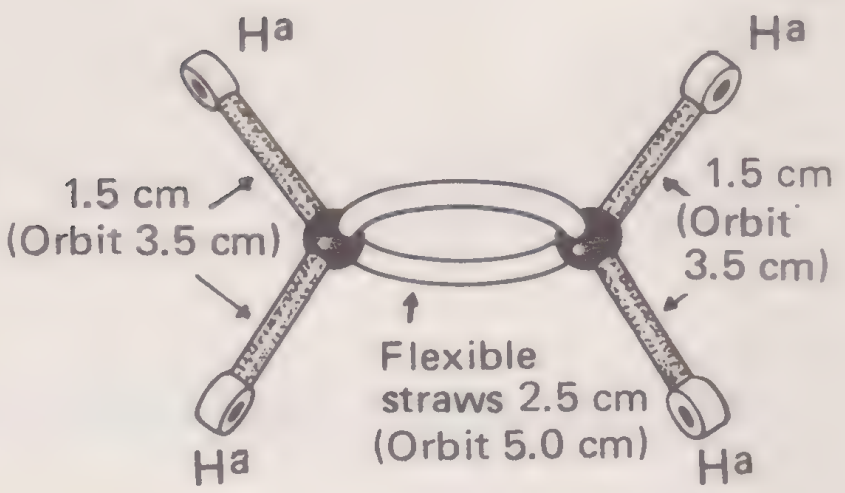


Figure 15 Ethene

3.1 *Do all the atoms lie in a plane?*

3.2 *Can the molecule be twisted?*

Measure the distance between the carbon centres.

3.3 *How does the length of the double bond in the model compare with that of C–C single bonds in earlier models?*

3.4 *How many electron pairs does each carbon atom have in ethene?*

3.5 *How many bonding electrons is this per carbon atom? Compare your answer to that for the carbon atoms in ethane (page 9).*

Derivatives of ethene

Remove one hydrogen centre from your model of ethene, and replace it by a chlorine centre, Cl^a, using a 3.5 cm (Orbit 5.0 cm) green straw. You now have chloroethene, C_2H_3Cl (known industrially as vinyl chloride).

3.6 *If you had chosen a different hydrogen atom for substitution by chlorine, would this have resulted in a different structure?*

3.7 *How many isomers of C_2H_3Cl are possible?*

Make up three models of chloroethene, C_2H_3Cl. Satisfy yourself that they are identical. (figure 16).

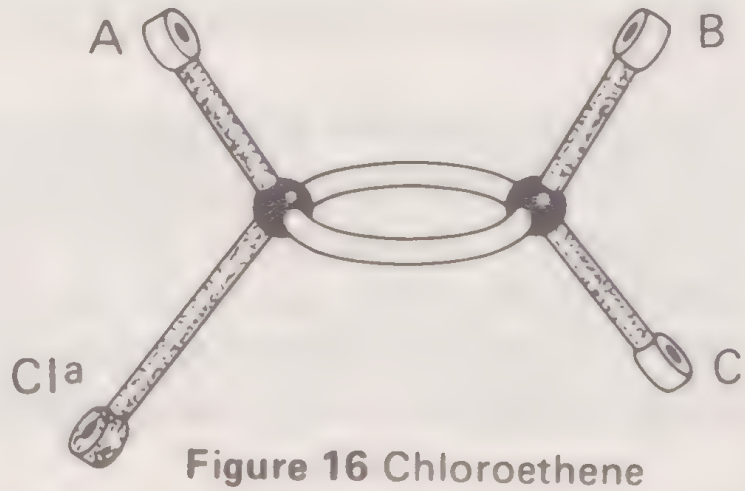


Figure 16 Chloroethene

Take the first model and substitute hydrogen centre A by a chlorine centre. Now take the second model, and substitute hydrogen centre B by chlorine. Finally take the third model and substitute hydrogen centre C by chlorine.

Call these three structures A, B and C respectively. They are all forms of dichloroethene, $C_2H_2Cl_2$, but they are not identical.

Model A has both chlorine atoms on carbon atom 1 and is called 1,1-dichloroethene. Models B and C both have their chlorine atoms on different carbon atoms: they are both named 1,2-dichloroethene. You will see however that B and C are different structures.

3.8 *Can you convert B into C by twisting, without breaking the double bond?*

3.9 *Disconnect one of the straws in the double bond: can you now convert B into C without breaking the other bond?*

Structures B and C represent what is known as geometric isomerism, which is a form of stereoisomerism. Geometric isomers have structures in which the atoms are similarly connected, but which differ as a result of restricted rotation of a bond in the molecule. If free rotation is made possible, one isomer may be converted into the other.

The isomer with both chlorine atoms on the same side is termed the *cis*-isomer (structure C) and the other structure is termed the *trans*-isomer (structure B). The complete name of structure C for instance is *cis*-1,2-dichloroethene.

Ethyne (acetylene)
Ethyne has a triple bond between its carbon atoms. Since there are no lone pairs on the carbon atoms, the configuration of the centres is linear.

Construct a model of ethyne using three 2.5 cm (Orbit 5.0 cm) flexible straws between carbon centres, C^k, as shown in figure 17. Note that considerable strain exists in the straws, representing the considerable reactivity of the C ≡ C bond. Also the bond is even shorter than C = C.

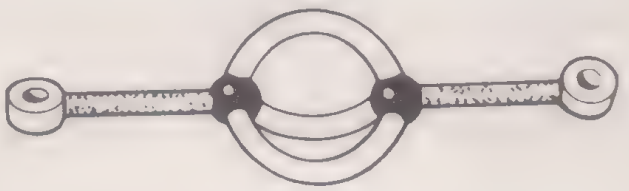


Figure 17 Ethyne

An alternative way of representing ethyne is to use linear C^b centres linked by a shortened rigid straw, say 2.0 cm (Orbit 4.0 cm) (figure 18).

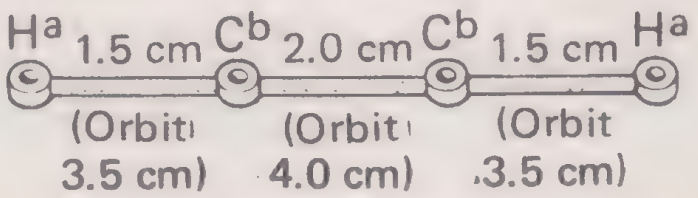


Figure 18

Petroleum cracking
The term 'cracking' means breaking up a large molecule into smaller fragments. Crude oil contains too many large molecules (lubricating oil etc) and not enough smaller molecules (motor fuel). A typical equation for a cracking process is:

$$C_{18}H_{38} \longrightarrow \underset{\text{octane}}{C_8H_{18}} + \underset{\text{octene}}{C_8H_{16}} + \underset{\text{ethene (ethylene)}}{C_2H_4}$$

Notice that in making octene a double bond links the two end C^k centres, using flexible 2.5 cm (Orbit 5.0 cm) straws, as in ethene.

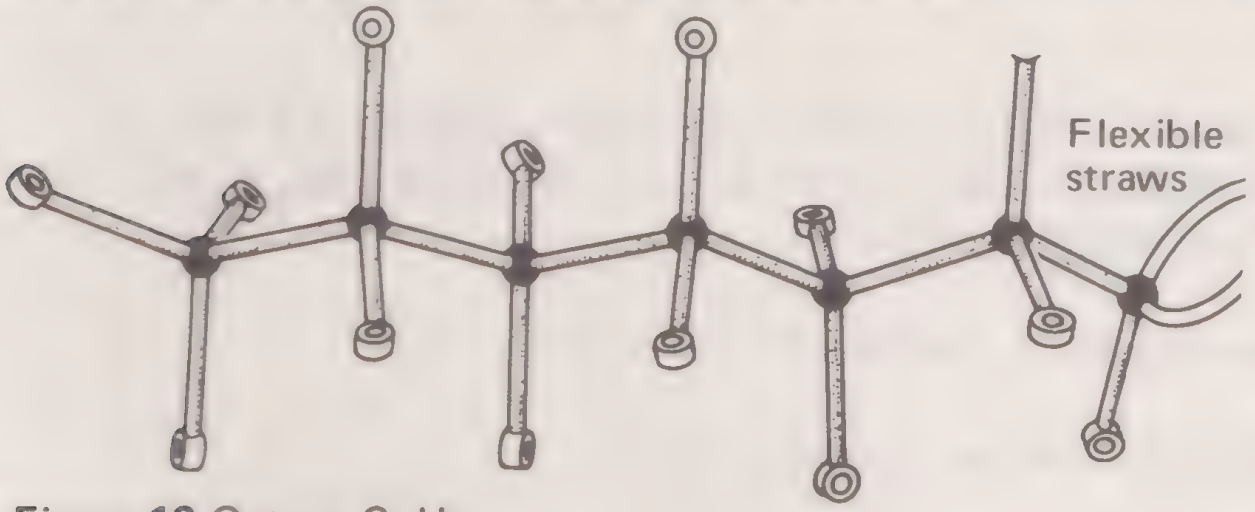


Figure 19 Octene C_8H_{16}

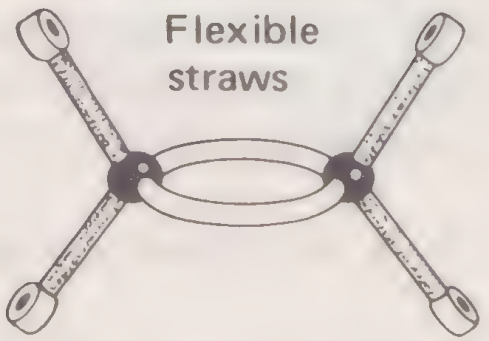


Figure 20 Ethene

Make models as shown in figures 19 and 20 to ill

4 Cyclic hydrocarbons

Simple cyclic structures

We have seen that so-called 'straight' chain hydrocarbons are in fact zig-zag structures that can be distorted by free rotation. The tetrahedral bond angle (approximately 110°) also allows a variety of ring structures to be made. Saturated hydrocarbons with rings in their structures are referred to as cycloalkanes.

Cyclopentane, C_5H_{10}

Take five tetrahedral carbon centres, C^k, and join them in a 'ring' using five 2.5 cm (Orbit 5.0 cm) green straws.

4.1 *Calculate the difference between the tetrahedral bond angle and the interior angle of the regular pentagon so formed.*

Notice at this stage that the carbon ring is completely planar. Now add ten 1.5 cm (Orbit 3.5 cm) green straws to the vacant prongs and attach ten hydrogen centres, H^a.

4.2 *Can the carbon-carbon bonds be freely rotated, as in a straight chain alkane? If not, why not?*

4.3 *How many isomers of 1,2-dichlorocyclopentane is it possible to make, in which the chlorine atoms are attached to* **adjacent** *carbon atoms?*

Cyclohexane, C_6H_{12}

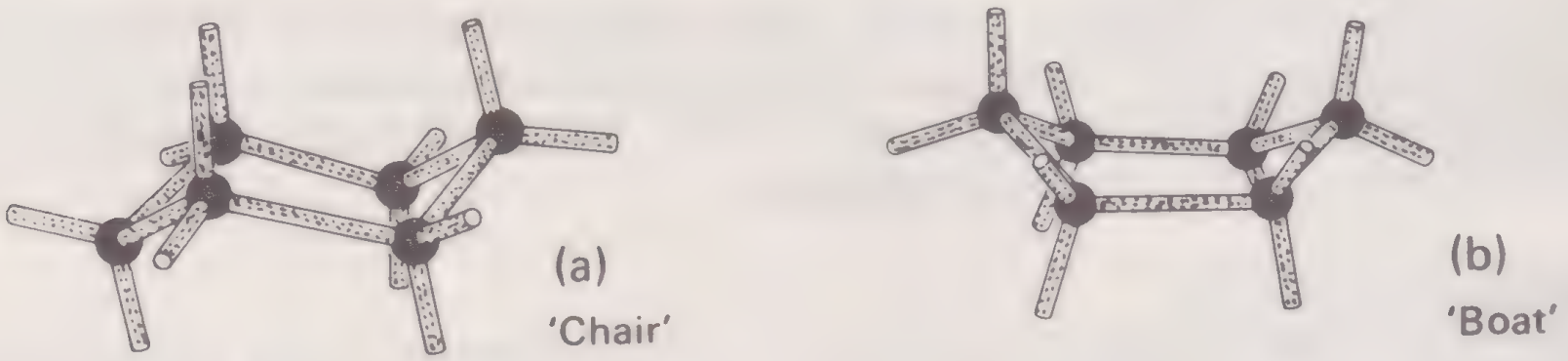
Take six tetrahedral carbon centres, C^k, and join them in a 'ring' using six 2.5 cm (Orbit 5.0 cm) green straws. Add twelve 1.5 cm (Orbit 3.5 cm) green straws to the vacant prongs and attach twelve hydrogen centres, H^a.

4.4 *Is the resultant ring structure planar or puckered?*

4.5 *What is the angle between adjacent carbon-carbon bonds?*

4.6 *Can the carbon-carbon bonds be (a) freely, or (b) slightly, rotated relative to one another?*

You will find that the six-membered ring is capable of two main shapes, or conformations. These are called the 'chair' form, figure 21(a), and the 'boat' form, figure 21(b), respectively. The hydrogen centres have been omitted from the figures for clarity.



(a) 'Chair'

(b) 'Boat'

Figure 21

Notice that a *slight* strain has to be applied to a given conformation in order to convert it into the other conformation, even though bonds do not have to be broken. In practice, cyclohexane consists of a mixture of conformations in dynamic equilibrium and it is not possible to separate them as they interconvert too readily.

Larger rings

Experiment now with larger ring structures, for instance cycloheptane, C_7H_{14} and cyclo-octane, C_8H_{16}. The 'crown' conformation of cyclo-octane, figure 22, is also the conformation taken up by the S_8 ring in the crystalline forms of sulphur.

4.7 *What is the bond angle between adjacent carbon atoms in cycloheptane and cyclo-octane?*

4.8 *It is not easy to synthesise very large rings of atoms, eg a C_{20} ring. Why should this be so?*

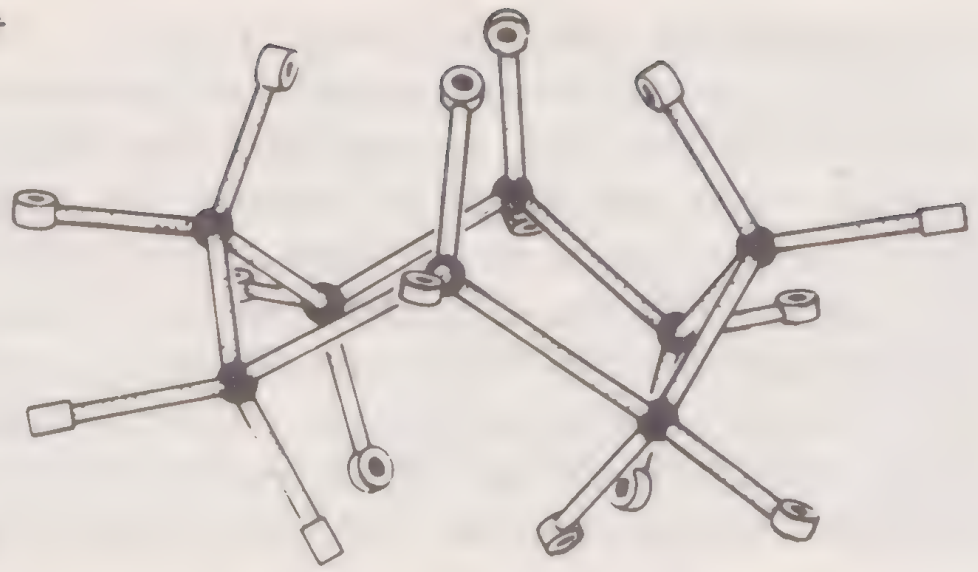


Figure 22 Cyclo-octane

Smaller rings

Using four tetrahedral carbon atoms and four 2.5 cm (Orbit 5.0 cm) flexible straws, make cyclo-butane, the ring structure C_4H_8.

4.9 *Why do you suppose that cyclobutane is unstable and quite reactive?*

The smallest ring, in cyclopropane (C_3H_6), can also only be made using flexible straws, and illustrates the same effect to an even more marked degree.

Summary

Saturated rings with five or more carbon atoms are unstrained. Saturated rings with six or more carbon atoms are non-planar, and can exist in more than one conformation. Saturated rings with four or less carbon atoms are strained due to distortion of bond angles from the tetrahedral positions. They are correspondingly reactive.

5 Functional groups in organic chemistry

This section summarizes some of the principal functional groups in organic chemistry by considering their function in a C_4-chain, butane.

Butane, $CH_3.CH_2.CH_2.CH_3$

You will need four C^k centres and ten H^a centres. Join the four carbon centres in a chain using 2.5 cm (Orbit 5.0 cm) green straws. Add the ten H^a centres using 1.5 cm (Orbit 3.5 cm) green straws. All the available prongs on the carbon centres will have been used up. This is a model of butane.

1-Chlorobutane, $CH_3.CH_2.CH_2.CH_2.Cl$

If butane and chlorine are mixed and allowed to react in diffused light, a number of products are obtained, among them the 1-chloro derivative. To illustrate this substitution reaction make a molecule of chlorine, Cl_2, by joining two Cl^a centres with a 2.5 cm (Orbit 5.0 cm) green straw. Now detach a hydrogen centre from an end carbon atom of the butane molecule, together with its 1.5 cm (Orbit 3.5 cm) green straw. Remove a chlorine centre from the model of the Cl_2 molecule (this illustrates the presence of a free chlorine atom, which is thought to participate in the substitution reaction). Attach the chlorine atom to the carbon chain with a 2.5 cm (Orbit 5.0 cm) green straw and attach the hydrogen atom to the free chlorine with the 1.5 cm (Orbit 3.5 cm) green straw.

$$CH_3.CH_2.CH_2.CH_3 + Cl_2 \longrightarrow CH_3.CH_2.CH_2.CH_2Cl + HCl$$

Butan-1 ol, $CH_3.CH_2.CH_2.CH_2OH$

If 1-chlorobutane is warmed with aqueous alkali, $OH^-(aq)$, a substitution reaction occurs. Make a model of the hydroxide ion, OH^-, using a two-pronged oxygen centre, O^d, with one free prong and one prong joined to an H^a centre with a 1.5 cm (Orbit 3.5 cm) green straw. Detach the chlorine centre from 1-chlorobutane and attach the OH-group.

$$CH_3.CH_2.CH_2.CH_2Cl + OH^- \longrightarrow CH_3.CH_2.CH_2.CH_2OH + Cl^-$$

Butanal, $CH_3.CH_2.CH_2.CHO$

If butan-1-ol is oxidized by distilling with dilute aqueous sodium dichromate, the end-group $-CH_2OH$ is oxidized to the group $-C(=O)H$

$$CH_3.CH_2.CH_2.CH_2OH + [O] \longrightarrow CH_3.CH_2.CH_2.CHO + H_2O$$

Construct a model of butanal using two 2.5 cm (Orbit 5.0 cm) flexible straws linking C^k with O^d to represent the carbonyl group, C=O.

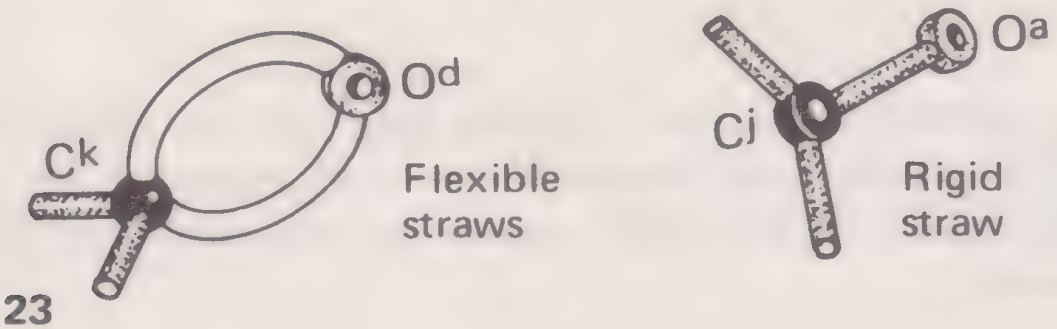


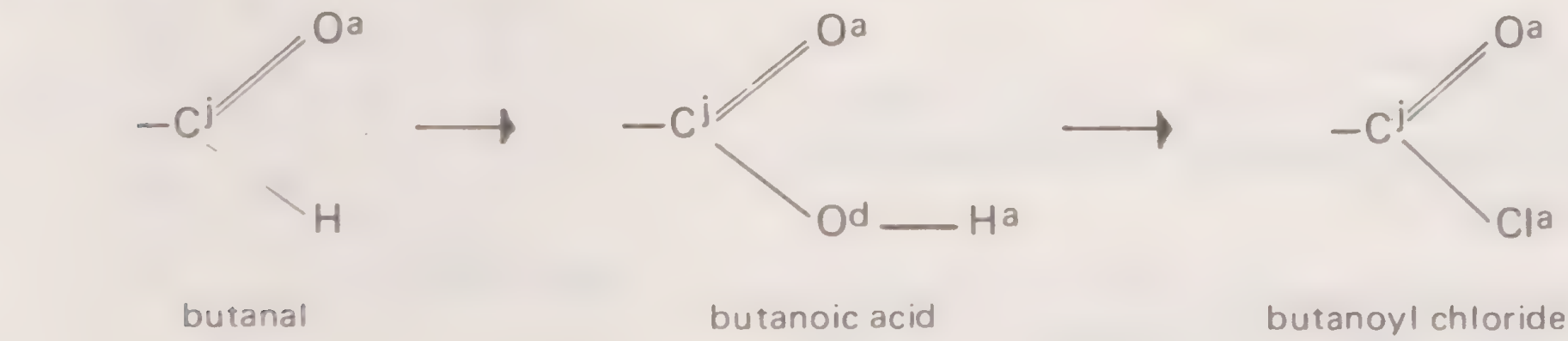
Figure 23

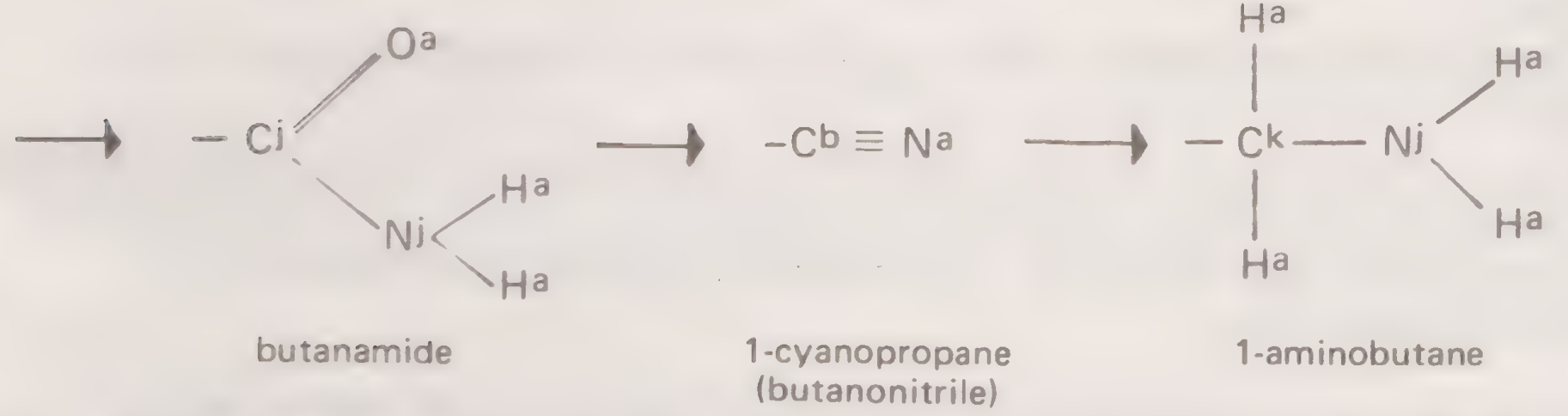
An alternative way of representing the carbonyl group is by using Cj and O^a centres linked by a 2.5 cm (Orbit 5.0 cm) rigid straw. In many ways this simplified representation is preferable, and in this booklet the use of flexible straws is confined to those double bonds where restricted rotation is important.

Figure 23 shows the alternative ways of making the carbonyl group.

Further functional groups

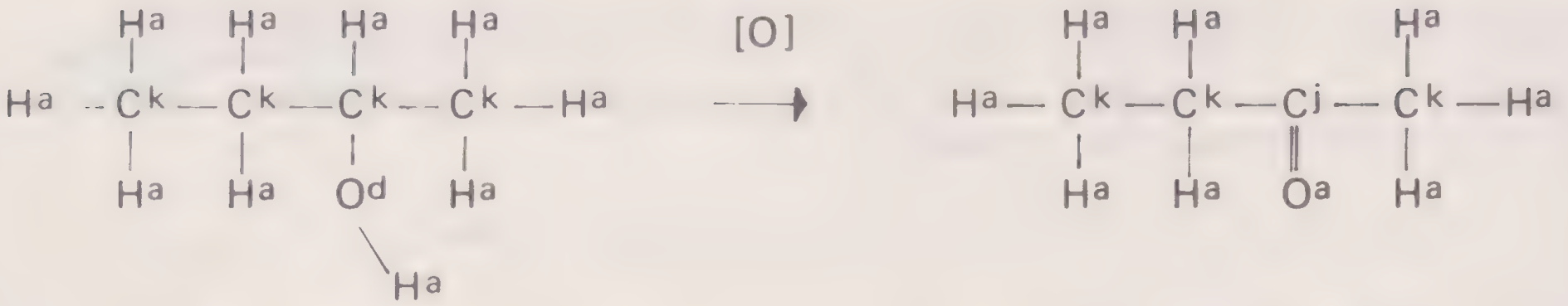
Using the same carbon chain, the following further stages in the synthetic route can be effected:





Secondary alcohols and ketones

If 2-chlorobutane is used in place of 1-chlorobutane as the starting material, aqueous alkali gives butan-2 ol, and oxidation of this gives butanone. Further oxidation cannot occur however without the carbon chain being broken.



butan-2-ol

butan-2-one

Isomers of butanol

Construct a model of butane, figure 24. In this molecule there are essentially two different types of hydrogen atom:

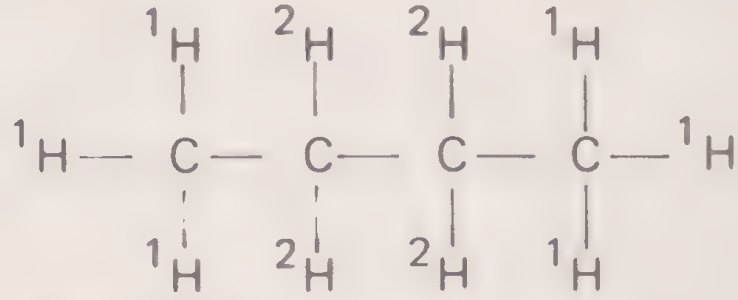


Figure 24 Butane

(a) Those attached to the end atoms, ie part of a methyl group, $-CH_3$ (labelled '1' on the diagram).
(b) Those attached to the other carbon atoms, ie part of a methylene group, $-CH_2-$, (labelled '2' on the diagram).

An alcohol may be regarded as derived from the parent hydrocarbon by the replacement of a hydrogen atom by a hydroxyl group, $-OH$. Construct a model of a hydroxyl group, use a two-bonded oxygen centre, O^d, with a hydrogen atom attached with a 1.5 cm (Orbit 3.5 cm) green straw.

5.1 *Why are the two bonds leading from the oxygen atom set at an angle instead of in a straight line?*

Two molecules of butanol exist, based upon the straight-chain hydrocarbon butane.

(1) Any one of the hydrogen atoms labelled '1' in figure 24 may be replaced by a hydroxyl group, making butan-1-ol, figure 25(a).

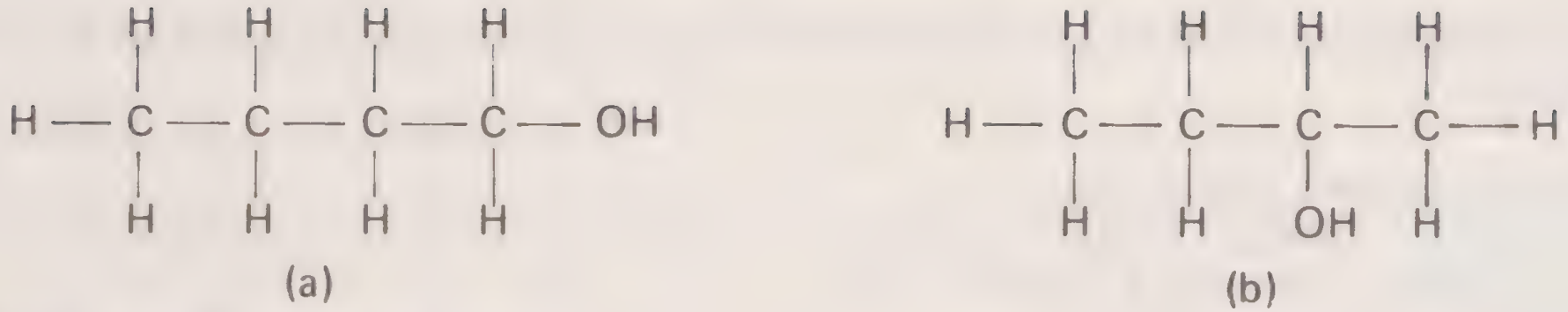


Figure 25 (a) Butan-1-ol, (b) Butan-2-ol

(2) Any one of the hydrogen atoms labelled '2' in figure 24 may be substituted by a hydroxyl group, making butan-2-ol, figure 25(b).

Construct models of the molecules in figures 25(a) and 25(b), using 2.5 cm (Orbit 5.0 cm) green straws to depict C—O bonds.

Further isomers of molecular formula $C_4H_{10}O$ can be made by taking the branched chain isomer of butane, and substituting different hydrogen atoms with a hydroxyl group.

5.2 *How many different 'kinds' of hydrogen atom are there in figure 26? (Examine each hydrogen atom in turn and see what it is attached to and what type of group it belongs to).*

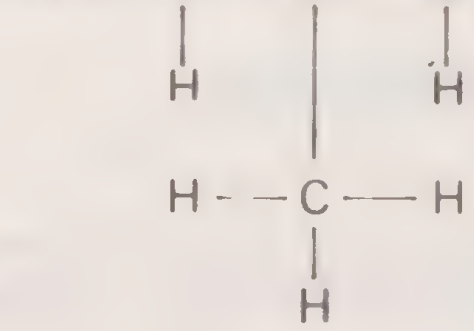


Figure 26 Methylpropane

Now construct models of the alcohols $C_4H_{10}O$ based upon the branched chain in figure 26.

Ethers of molecular formula $C_4H_{10}O$

If you have reasoned correctly so far, you should have managed to construct four different models of alcohols (substances containing the hydroxyl group, —OH) of molecular formula $C_4H_{10}O$; two based upon the straight chain of carbon atoms and two upon the branched chain.

This however does not represent all the possible ways of connecting together the atoms $C_4H_{10}O$. A further series of models can be constructed, containing the link C – O – C.

Such compounds consist of two alkyl groups linked to an oxygen atom and are known as ethers.

Figure 27 shows a simple ether ethoxyethane, which is isomeric with the butyl alcohols. Construct a model of this, using a bent oxygen centre O^d.

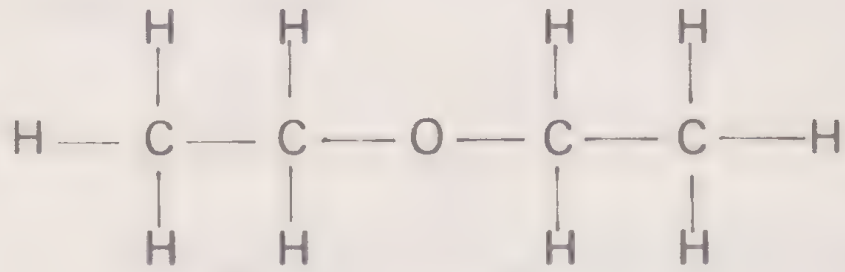


Figure 27 Ethoxyethane

5.3 *How many other ethers can be made, of the same molecular formula, ie isomeric with ethoxyethane? Try to predict the possibilities on paper, and then construct models. Check carefully to see that you have not made two the same.*

Definitions
(1) The relationship between compounds of the same molecular formula but containing different functional groups is sometimes known as functional group isomerism.
(2) The relationship between isomers which differ only in the nature of their alkyl groups attached to a given group is sometimes known as metamerism.

Further suggestions
Use the model kit to help answer the following questions:

5.4 *How many isomers of molecular formula C_3H_8O are possible? How many of these are alcohols, and how many ethers?*

5.5 *How many isomers of molecular formula $C_5H_{12}O$ are possible? Try to work this out on paper, and check your predictions by constructing models.*

6 Benzene and its derivatives

Benzene, C_6H_6
The true shape of the benzene molecule is a regular hexagon, with 120° bond angles throughout. An approximation to its structure may be obtained by constructing a ring using six C^k centres linked alternately by double and single bonds. Six hydrogen centres H^a are then joined to the remaining prongs (figure 28).

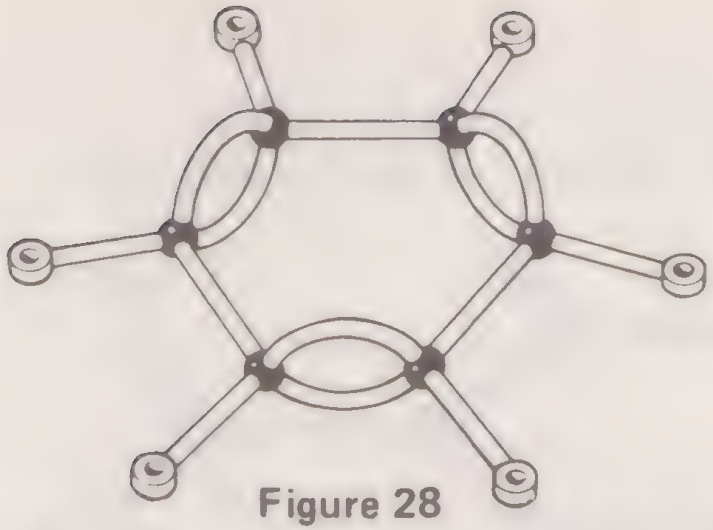


Figure 28

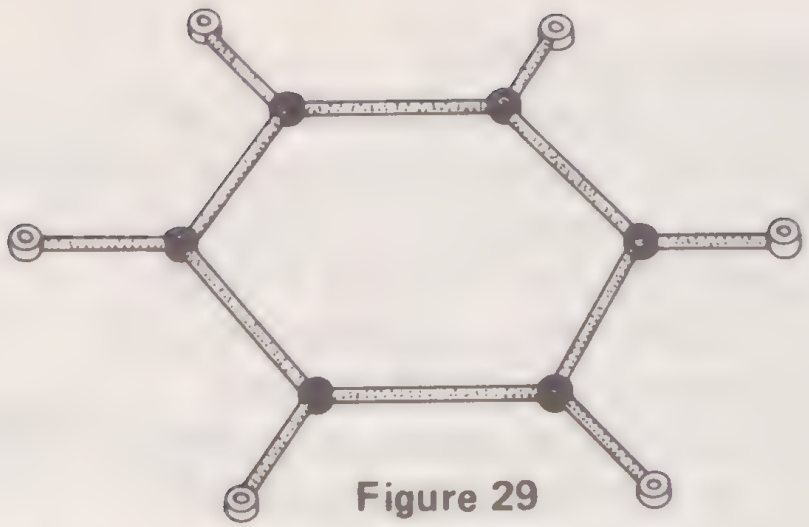


Figure 29

A better representation is to use six trigonal carbon centres C^{J} in the form of a planar ring, joined by 2.5 cm (Orbit 5.0 cm) green straws, with six hydrogen centres attached to the remaining prongs with 1.5 cm (Orbit 3.5 cm) green straws (figure 29).

In this model, the 2.5 cm (Orbit 5.0 cm) green straws represent C—C bonds.

Chlorobenzene, C_6H_5Cl

Detach one hydrogen centre, together with its bond, from your benzene model, and attach a chlorine centre, Cl^{a}, with a 2.5 cm (Orbit 5.0 cm) green straw. This is a model of chlorobenzene.

6.1 *Is isomerism of chlorobenzene possible, assuming the benzene ring to be always present?*

Dichlorobenzene, $C_6H_4Cl_2$

Detach another hydrogen centre (any one will do) from your chlorobenzene model, and replace with chlorine as before. You now have a model of one of the isomers of dichlorobenzene.

6.2 *How many possible isomers exist for dichlorobenzene?*

Make models of as many isomers as you can and check carefully (by rearranging them and turning them over) that they are all different. Figure 30 shows one possibility, and its name. What are the others?

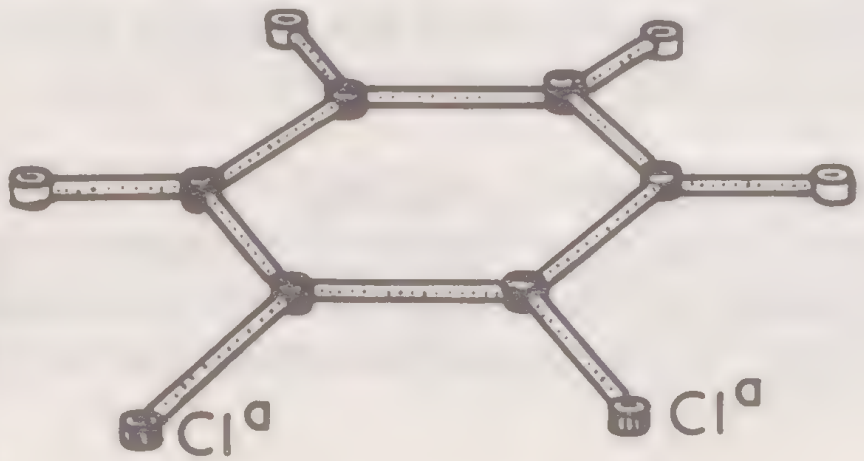


Figure 30 1,2-Dichlorobenzene

Nitrobenzene, $C_6H_5NO_2$

The action of nitronium ion, NO_2^+, present in a mixture of concentrated nitric and sulphuric acids, converts benzene to nitrobenzene. The nitro group, $-NO_2$ has no lone pairs on the nitrogen atom and therefore has a trigonal centre N^j. Make a nitro group by joining two oxygen centres O^a to the nitrogen centre with 2.5 cm (Orbit 5.0 cm) green straws, and attach this group to the benzene ring with a 2.5 cm (Orbit 5.0 cm) green straw, having first removed a hydrogen atomic centre.

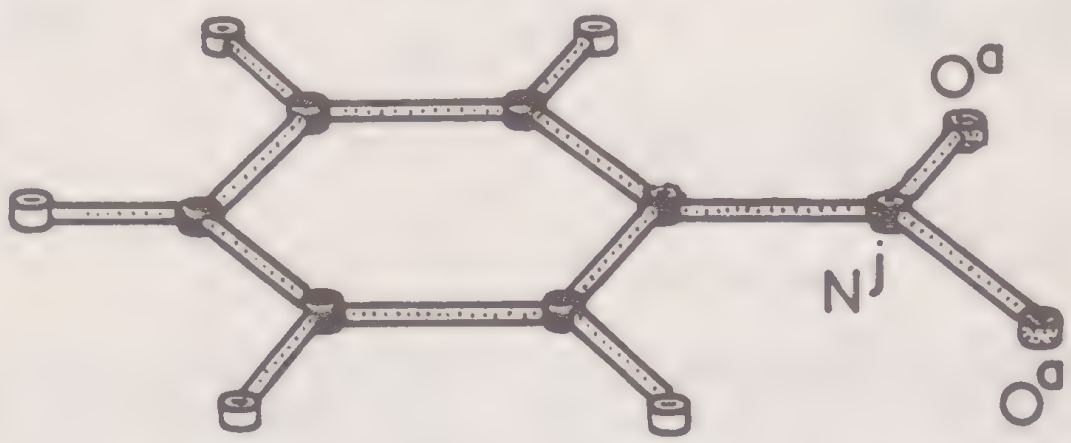


Figure 31 Nitrobenzene

The carbon-nitrogen bond does in fact have some π-bond character, due to interaction of the π-electrons in the carbon ring with the nitrogen atom.

6.3 *How many isomers of dinitrobenzene, $C_6H_4(NO_2)_2$, are possible? Name them.*

Phenylamine (aniline) $C_6H_5NH_2$

Reduction of nitrobenzene in strongly acid conditions gives the phenylammonium ion, $C_6H_5NH_3^+$.

6.4 *What will be the probable configuration of the bonds around the nitrogen atom in $C_6H_5NH_3^+$? Will a π-bond between the carbon and nitrogen atoms be possible?*

Make a model of the phenylammonium ion, using the correct nitrogen centre, with 1.5 cm (Orbit 3.5 cm) green straws to represent N—H bonds, and a 2.5 cm (Orbit 5.0 cm) green straw for the C—N bond.

Methylbenzene, $C_6H_5CH_3$

Hydrocarbon derivatives of benzene are present in coal tar. The simplest is methylbenzene. To make a model, start with benzene and replace a hydrogen centre with a methyl group $-CH_3$. Use a tetrahedral carbon centre, C^k, for the methyl group.

6.6 *How many isomers containing a benzene ring exist corresponding to the molecular formula C_8H_{10}? Make models, and name them.*

Phenol, C_6H_5OH

The oxygen atom in phenol possesses two lone pairs and its configuration is therefore bent (page 8). Construct a hydroxyl group —OH using an oxygen centre O^d joined to a hydrogen centre H^a using 1.5 cm (Orbit 3.5 cm) green straws. Take a model of benzene, remove a hydrogen atom and attach a hydroxyl group using a 2.5 cm (Orbit 5.0 cm) green straw.

Benzenesulphonic acid, $C_6H_5SO_2OH$

Benzenesulphonic acid may be regarded as derived from sulphuric acid (page 41) by the replacement of a hydroxyl group in the latter by a phenyl group, $-C_6H_5$. Construct a model of sulphuric acid, H_2SO_4, and then remove a hydroxyl group from it. Remove a hydrogen centre from a model of benzene. Join the two resultant groups with a 2.5 cm (Orbit 5.0 cm) green straw.

Benzenecarboxylic acid (Benzoic acid), C_6H_5COOH

Benzenecarboxylic acid contains the carboxyl group, which comprises a carbonyl group joined to a hydroxyl group. Construct a carbonyl group, using a trigonal carbon centre, C^j, joined to an oxygen centre O^a with a 2.5 cm (Orbit 5.0 cm) green straw. Join this group to a hydroxyl group with a 2.5 cm (Orbit 5.0 cm) green straw. The complete structure of benzenecarboxylic acid is made by removing a hydrogen atom from a model of a benzene molecule, and connecting instead the carboxyl group with a 2.5 cm (Orbit 5.0 cm) green straw.

7 Polymerization

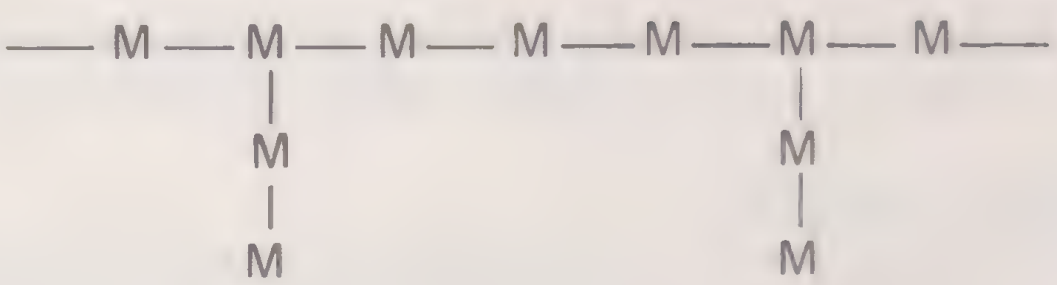
Introduction

Polymers are macromolecules built by the linking together of monomer units. The following are some of the ways in which monomers (represented by M and N) can be linked together.

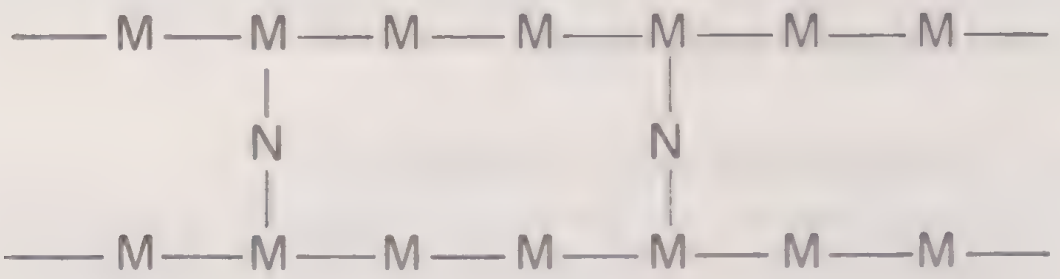
(i) Simple linear polymer —M—M—M—M—M—M—M—

(ii) Simple linear co-polymer —M—N—M—N—M—N—M—

(iii) Simple cross-linked polymer



(iv) Cross-linked co-polymer



Simple linear polymers

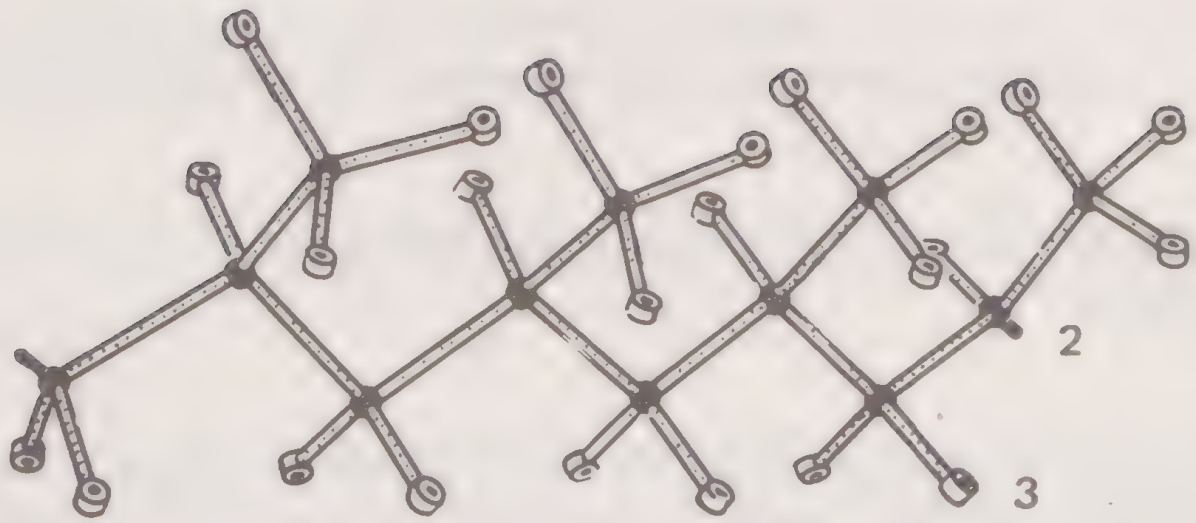
Polyethene (polythene) is formed by the addition polymerization of ethene (page 12). Similarly, tetrafluoroethene, C_2F_4, polymerizes to give polytetrafluoroethene, PTFE, $(C_2F_4)_x$.

To make models of these two simple polymers, start by constructing a chain of carbon atoms, using tetrahedral carbon centres, C^k, linked by 2.5 cm (Orbit 5.0 cm) green straws. For polythene, connect hydrogen centres, H^a, to the unoccupied carbon prongs, using 1.5 cm (Orbit 3.5 cm) green straws. For PTFE, connect green centres (Cl^a will serve here) using 2.5 cm (Orbit 5.0 cm) green straws.

Polypropene is the addition polymer made by the polymerization of propene, $CH_3{-}CH = CH_2$. The monomer is made by constructing ethene, C_2H_4, as described on page 12, and then substituting one hydrogen centre with a methyl group, $-CH_3$. The methyl group uses a tetrahedral centre, C^k, linked to three hydrogen centres by 1.5 cm (Orbit 3.5 cm) green straws.

Compounds of the general formula $CH_2 = CH_2X$ can be polymerized to give two different forms each having a regular structure. Figure 32 shows (a) the *isotactic* form, in which all the X groups (in these figures X is a methyl group) lie on the same side of the polymer chain; (b) the *syndiotactic* form, in which the X groups lie on alternate sides. There is a third form, the *atactic* form, in which the X groups are arranged at random.

(a)

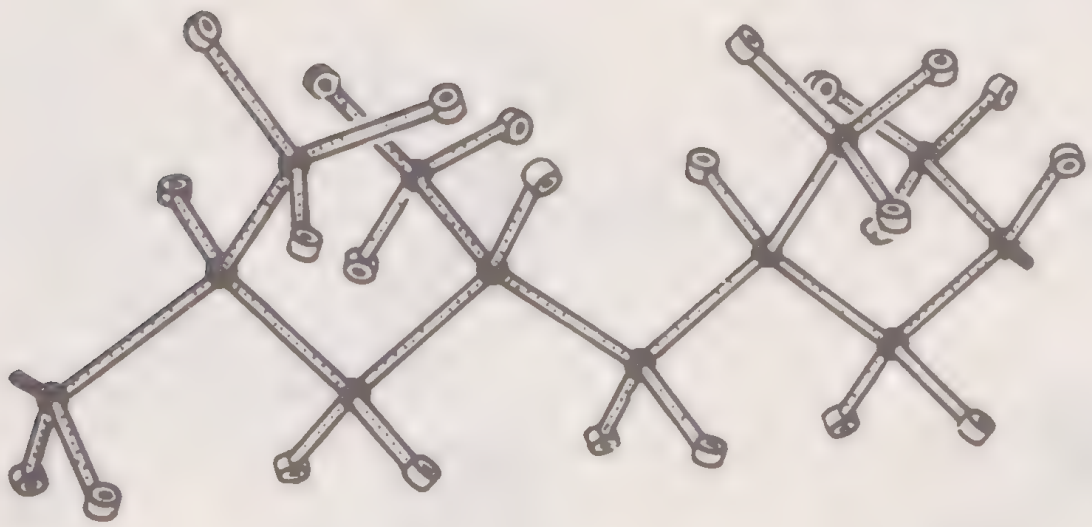


1 = X

2 = carbon atoms

3 = hydrogen atoms

(b)



(c)

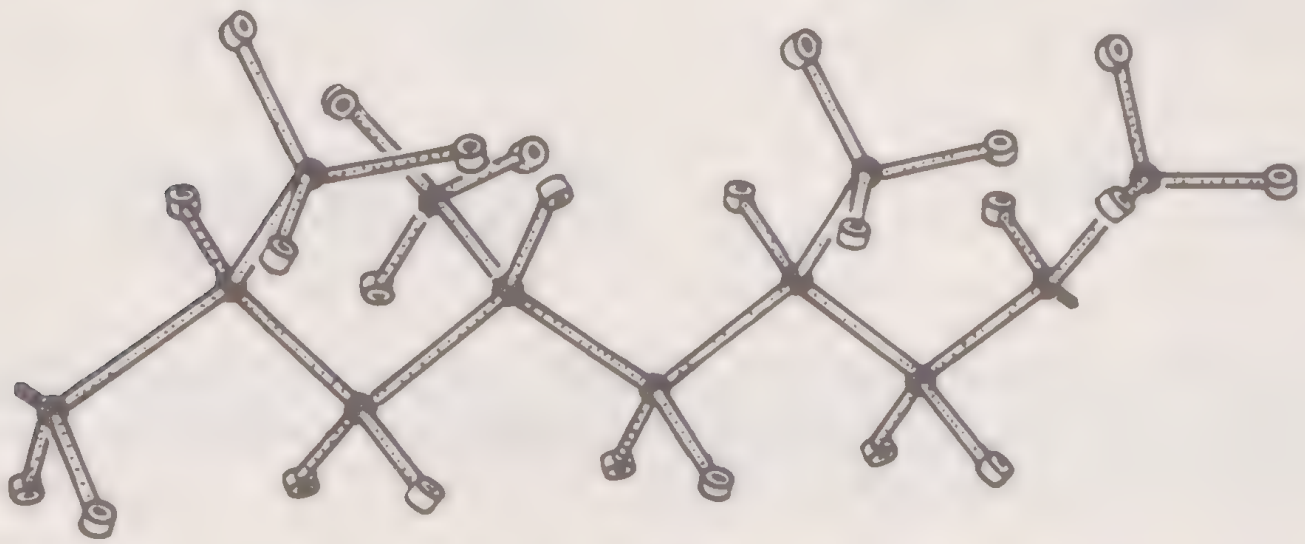


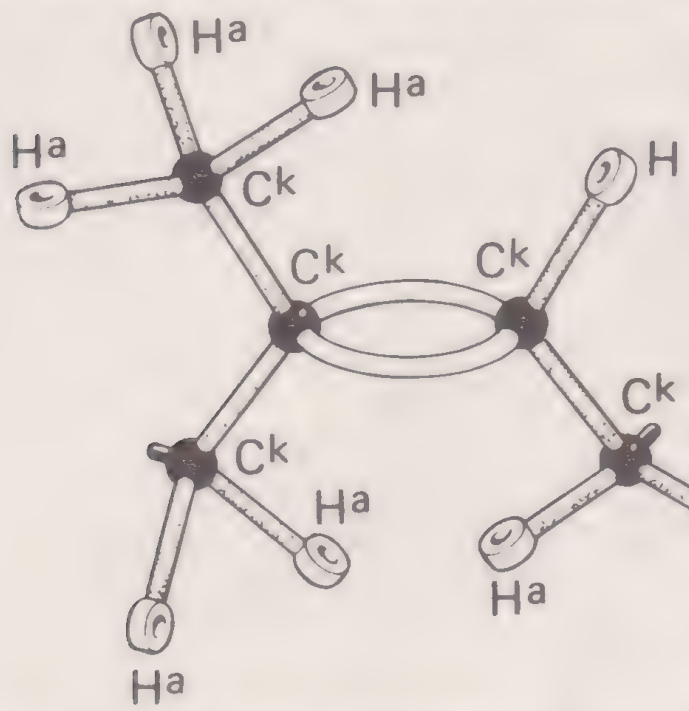
Figure 32 Polymers (a) *isotactic,* (b) *syndiotactic,* (c) *atactic*

Polypropene is made in forms (a) and (c), where X = methyl. To make models of the forms, start with a model of polythene, and replace hydrogen atoms with methyl groups as in figure 32.

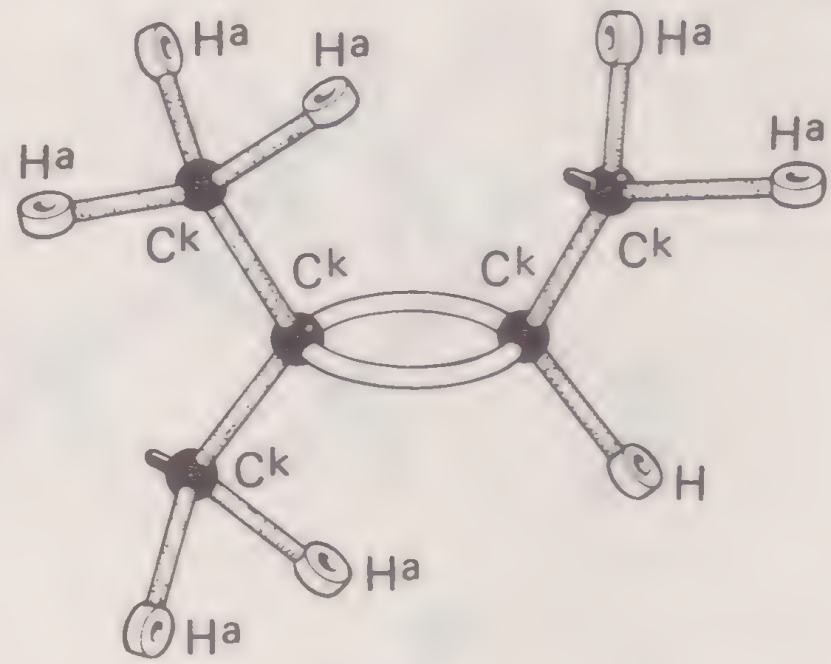
Note that these polymers all have saturated structures and hence are all highly unreactive compared with their monomers.

Synthetic rubbers

Natural rubber is an *elastomer,* containing molecules made up on average of about 10^4 units of isoprene, $CH_2{=}C(CH_3){-}CH{=}CH_2$. Isoprene can also be polymerized synthetically in isotactic form. The double bonds rearrange themselves and the linking bonds may be either *cis* or *trans* to one another (page 14).



(a) *cis*-isoprene, which corresponds closely to natural rubber



(b) *trans*-isoprene, which corresponds closely to gutta percha

Figure 33

Make models of the monomer units (a) and (b), using C^k centres and flexible straws where indicated. Use 2.5 cm (Orbit 5.0 cm) green straws for carbon-carbon bonds, and 1.5 cm (Orbit 3.5 cm) green straws for bonds to hydrogen.

To make a model of natural rubber, connect several units (a) together. The elastic property of rubber is due to weak attractive forces between adjacent chains, coupled with a small degree of cross-linking.

Nylon—a co-polymer

The term 'Nylon' embraces several different condensation co-polymers of a similar type. One form, Nylon 6—6, is made by the condensation reaction between molecules of 1,6-diaminohexane $H_2N.(CH_2)_6.NH_2$, with hexane-1,6 dioyl chloride (adipyl chloride), $Cl.CO.(CH_2)_4.CO.Cl$, with the elimination of hydrogen chloride. The repeating unit is $-NH.(CH_2)_6.NH.CO.(CH_2)_4.CO-$. Figure 34 shows a model of the unit. Use 2.5 cm (Orbit 5.0 cm) green straws for all bonds except those to hydrogen atoms which require 1.5 cm (Orbit 3.5 cm) bonds.

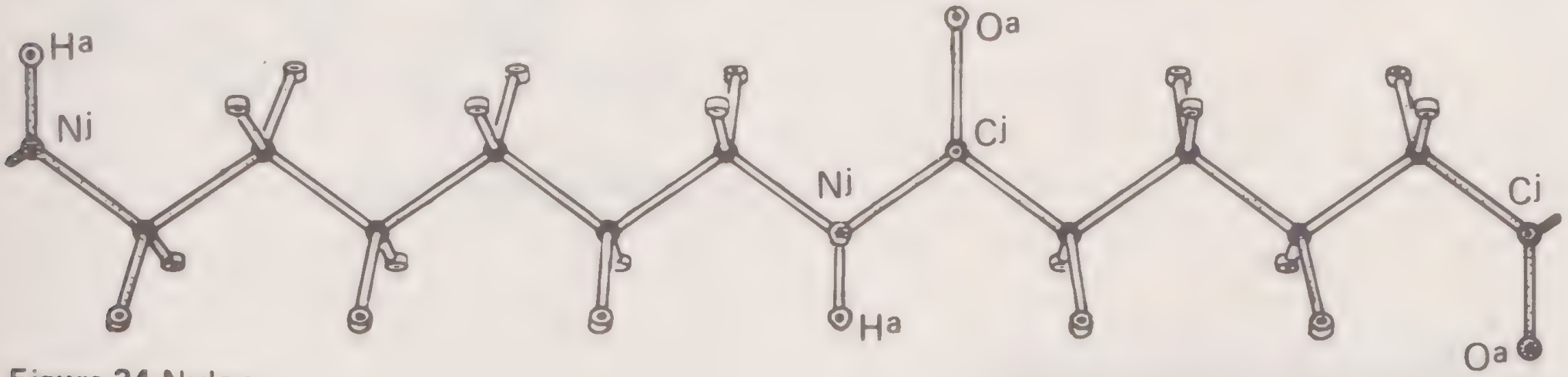


Figure 34 Nylon

Perspex

Figure 35 shows you how to make a model of the 'Perspex' monomer, methyl methacrylate. The active double-bond is shown using flexible straws, just as with ethene.

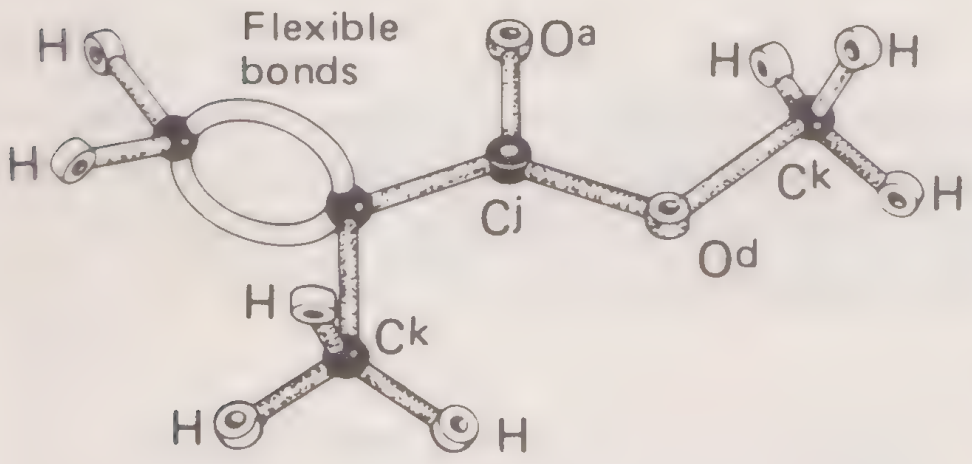


Figure 35 Perspex monomer

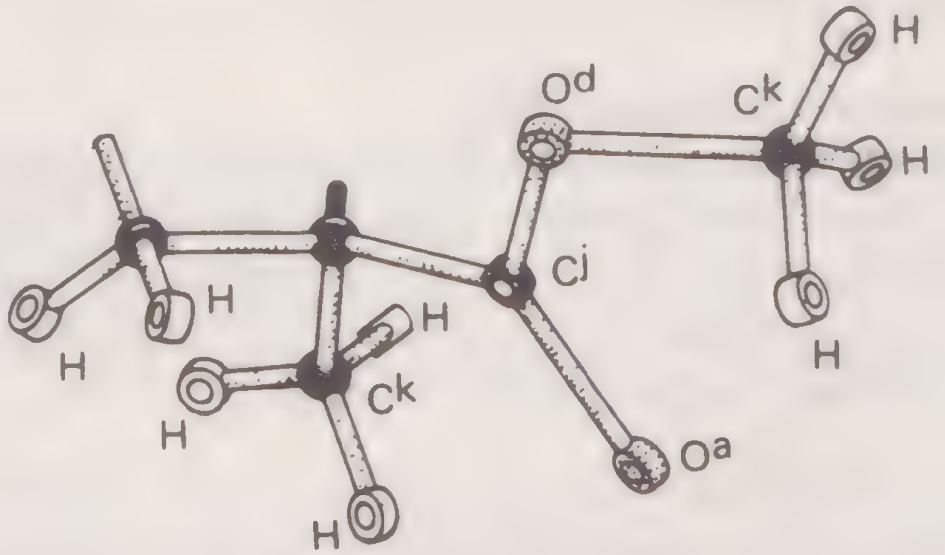


Figure 36 'Activated' perspex monomer

Figure 36 shows a way in which you can represent the 'Perspex' monomer after it has been activated by the catalyst.

Now, to make the model of the polymer 'Perspex' make two or three such monomer units and join them together to form a long chain, as shown in figure 37.

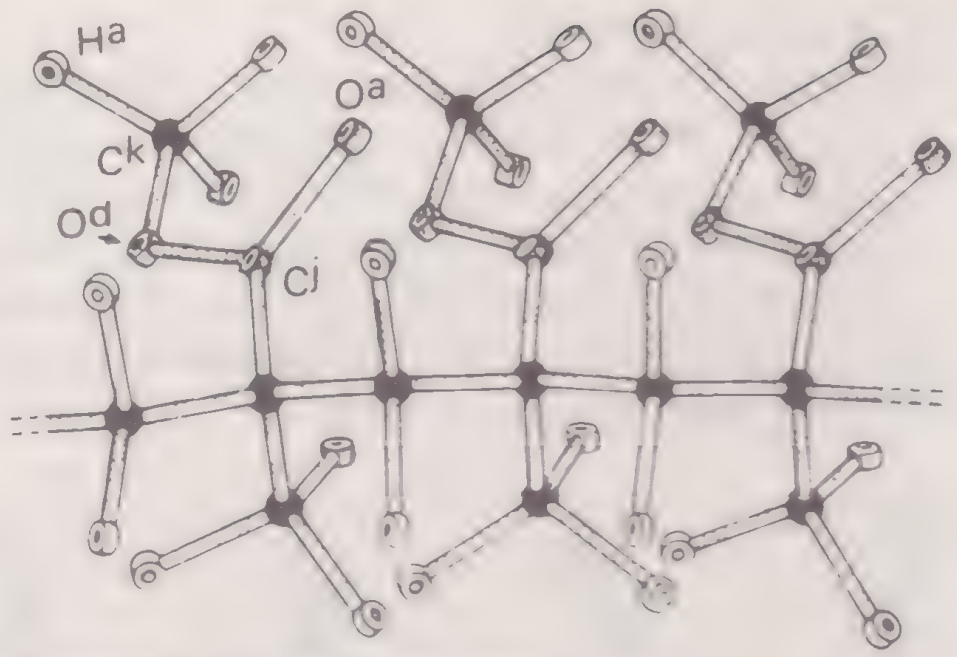


Figure 37 Perspex polymer

8 Optical isomerism

Introduction

When a molecule has a structure with no centre or plane of symmetry, it is said to be *asymmetric.* Substances whose molecules are asymmetric show *optical activity*, that is, they can rotate the plane of polarization of light, if a polarized beam is passed through a solution containing the substance.

Asymmetric carbon atoms

Although the phenomenon of optical activity is not confined solely to carbon compounds it is very common here. To illustrate the effect take a tetrahedral carbon atom, C^k, and attach four 2.5 cm (Orbit 5.0 cm) green straws. Now take any four differently coloured atoms and attach them to the straws in any relative position you like. The result illustrates an asymmetric molecule.

To demonstrate the asymmetry, make a second model *identical* with the first in every respect. Now take any two of the coloured atoms in the second model and exchange their positions. The second model is now the same as the first in all respects but one; it is the mirror image.

Take a piece of plane mirror large enough to enable you to view the entire reflection of one of the models, and place it vertically next to one of the models as in figure 38. Now adjust the second model so that it coincides exactly with the virtual image of the first model.

Two substances that are related in this mirror image fashion are said to be *optical isomers, or enantiomers.* Optical isomerism is a form of stereoisomerism, (page 14).

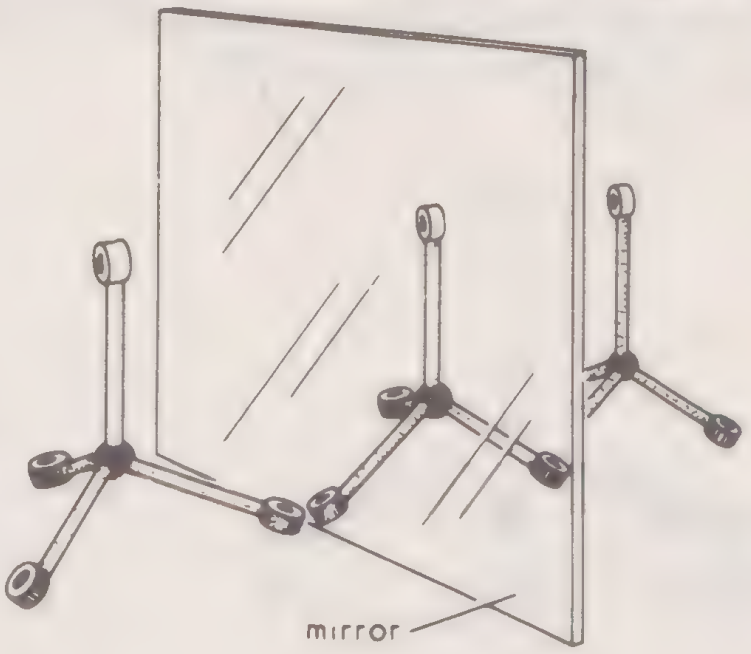


Figure 38

8.1 *Is it possible to rotate the position of the second model to make it appear identical with the first, without exchanging any groups?*

8.2 *Try to think of pairs of everyday objects that are related in the same way as stereoisomers.*

8.3 *Does chlorofluoromethane, CH_2FCl, show optical activity?*

To answer question 8.3, make a model of the molecule, set up the mirror as in figure 38, and then construct a second model to coincide with the mirror image of the first. Then find whether the pair of models are in fact identical by rotating them to see if their groups can be made to coincide.

For the molecule to be asymmetric and hence to show optical activity, there must be four different groups attached to the central carbon atom. In the case of CH_2FCl, two of the groups are identical (ie the two hydrogen atoms) and hence the substance is optically inactive.

Lactic acid (2-hydroxypropanoic acid)

To make instructions easier, the bonds are drawn in perspective in drawings of asymmetric molecules. Where a bond is shown thicker at one end than the other, the thicker end is taken to be closer to the observer. Using this convention, construct models of the two forms of lactic acid shown in figure 39.

Figure 39 (a) D-lactic acid, (b) L-lactic acid

Use 1.5 cm (Orbit 3.5 cm) straws for the C—H and O—H bonds, and 2.5 cm (Orbit 5.0 cm) straws for the other bonds. The carboxyl group, —COOH in figure 39, is constructed as shown in figure 40.

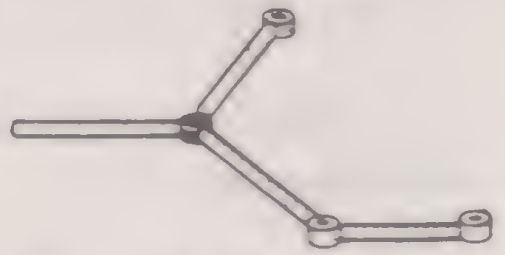


Figure 40 Carboxyl group

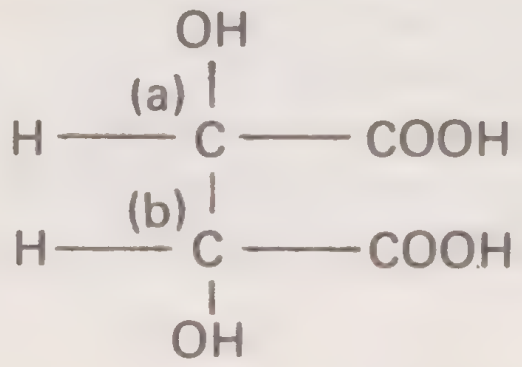
Figure 39(a) is called D-lactic acid.
Figure 39(b) is L-lactic acid which has the opposite effect on the plane of polarized light. A 50:50 mixture of the two forms in solution has no effect on the plane of polarized light, and is called a *racemic mixture.*

8.4 *Is the carbon atom of the carboxyl group, COOH, asymmetric and capable of causing optical activity in a molecule? Make a model of hydroxyethanoic acid, $CH_2OH.COOH$, and check whether it is asymmetric.*

Optically active substances occur very commonly in living materials. For instance D-lactic acid is produced in muscle and is obtained from meat extract. L-lactic acid does not occur naturally. In general, L-isomers are uncommon in nature

Molecules with two asymmetric carbon atoms

Tartaric acid (2,3-dihydroxybutanedioic acid) has the structure



Note that both the carbon atoms (a) and (b) are asymmetric, ie they are each linked to four different atoms or groups. When a molecule has more than one asymmetric centre, further optical isomers are possible. To find out how many, proceed as follows.

Make four models of one end of the tartaric acid molecule, as in figure 41(a). Call these 'left-handed'. Now make four 'right-handed' forms as illustrated in figure 41(b).

Now join up the halves as follows:

(1) left-hand joined to right-hand form; make two models thus.
(2) left-hand joined to left-hand form.
(3) right-hand joined to right-hand form.

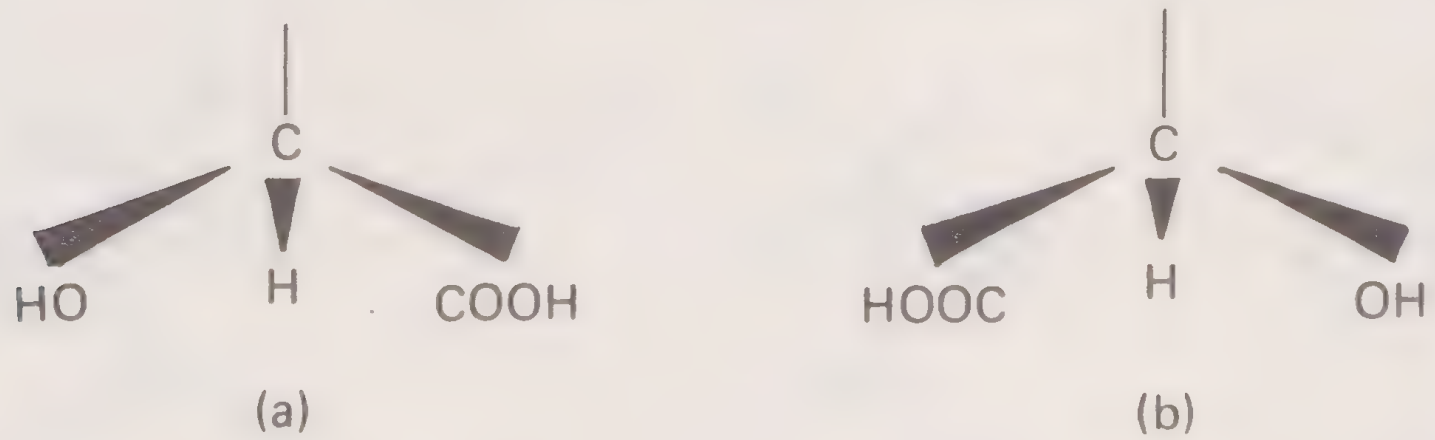


Figure 41

Take model (2) and place it next to a mirror, just as you did with the simple model described on page 31. Now take model (3) and place it behind the mirror. Adjust the relative positions of the groups so that the mirror image of (2) coincides exactly with (3). Note that in order to do this you may have to rotate the groups around the carbon-carbon bonds, and you may also have to rotate the carboxyl and hydroxyl groups themselves. (figure 42).

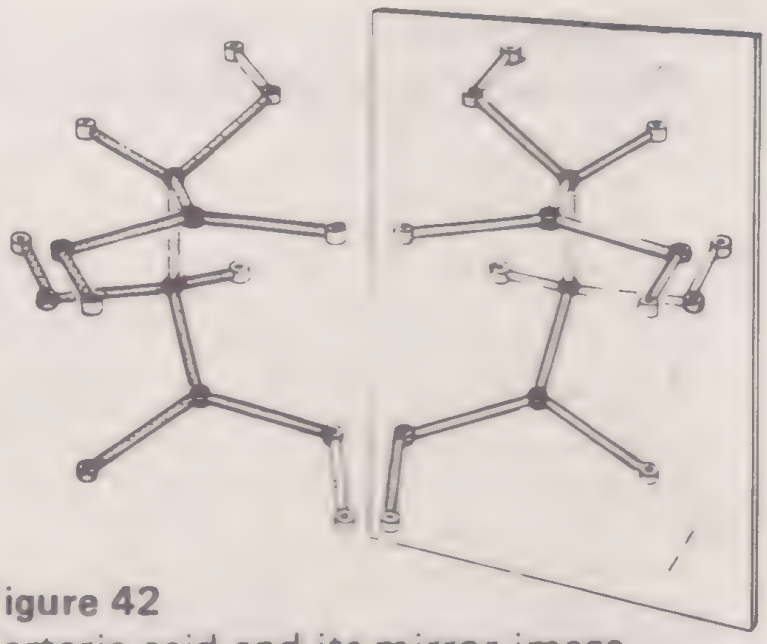


Figure 42
Tartaric acid and its mirror image

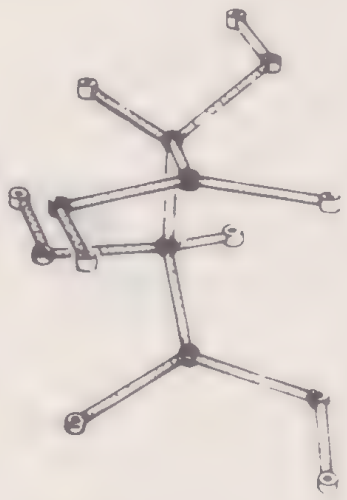
Configurations (2) and (3) are optically active forms of tartaric acid, ie solutions of each have equal and opposite effects on the plane of polarized light.

Now take your two models made as in (1). Place one by the mirror and attempt to arrange the other so that it coincides with the mirror image of the first. As before, it may be necessary to rotate the groups, but it is important not to disconnect any bonds.

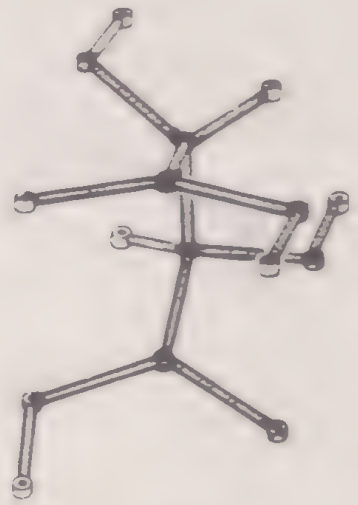
Model (1) can be superimposed on its mirror image despite the fact that it has two asymmetric carbon atoms. The reason is that one end of the molecule is a mirror image of the other end, and the molecule as a whole has a plane of symmetry. (1) is known as the *meso* form: since the whole molecule is not asymmetric, it does not rotate the plane of polarized light. Figure 43 illustrates the three forms of tartaric acid.

Figure 43

Model (1)
meso tartaric acid



Model (2)
L-tartaric acid



Model (3)
D-tartaric acid

There is a fourth form of tartaric acid, the racemic acid produced by crystallizing tartaric acid from an equimolar mixture of the optically active forms (2) and (3). Its composition may be represented as one mole of each form plus two moles of water of crystallization.

The chemical properties of the D and L modifications of tartaric acid are identical. The physical properties (except for the action on polarized light) are also identical.

8.5 *There are two acids corresponding to the formula HOOC.CH=CH.COOH, depending on whether the carboxyl groups are cis or trans to the double bond.*
Use models to predict which form of tartaric acid each will produce on oxidation with dilute potassium permanganate solution:

$$HOOC.CH=CH.COOH + [O] + H_2O \rightarrow HOOC.CHOH.CHOH.COOH$$

Assume that the two hydroxyl groups are added from the same side of the double bond.

Summary

Stereoisomerism can be subdivided into geometrical isomerism and optical isomerism.

For a molecular substance to be optically active, it must possess molecules with no plane or centre of symmetry. Such molecules are non-superimposable on their mirror images.

A carbon atom becomes asymmetric if it is attached to four different groups.

Where two asymmetric centres exist in a molecule, it is possible for the molecule as a whole to possess a plane of symmetry and be optically inactive.

9 Simple inorganic molecules

Carbon dioxide, CO_2

The carbon atom in carbon dioxide contains two double bonds and no lone pairs.

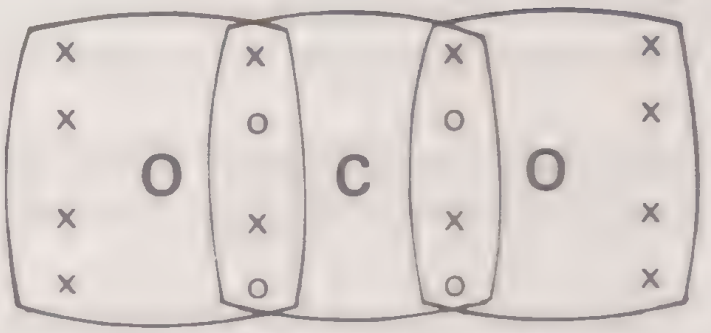


Figure 44 Carbon dioxide

Its shape is therefore linear, unlike H_2O which is bent (page 6). CO_2 has no lone pairs to distort its shape. To construct a model link a C^k centre to two O^d centres using 2.5 cm (Orbit 5.0 cm) flexible straws, (figure 45).

A simpler representation is to use rigid green straws linking a linear C^b centre to two O^a centres (cf simplified representation of carbonyl group, page 18).

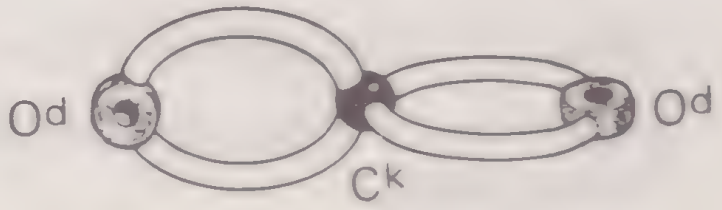


Figure 45 Carbon dioxide

9.1 *Carbon disulphide is a volatile liquid of molecular formula CS_2. Suggest a structure and electronic configuration for it, and make a model.*

Carbonic acid, H_2CO_3

A solution of carbon dioxide in water contains carbonic acid, H_2CO_3. The electronic configuration of the carbon atom is similar to that in ethene (page 12) with three bonds and no lone pairs. To make a model, take a trigonal carbon centre, C^j, and connect two oxygen centres O^d, and one oxygen centre O^a, with 2.5 cm (Orbit 5.0 cm) green straws. Connect hydrogen centres to the oxygen centres O^d, with 1.5 cm (Orbit 3.5 cm) straws. The carbonate ion, CO_3^{2-}, is completely symmetrical with 120° angles between all C—O bonds.

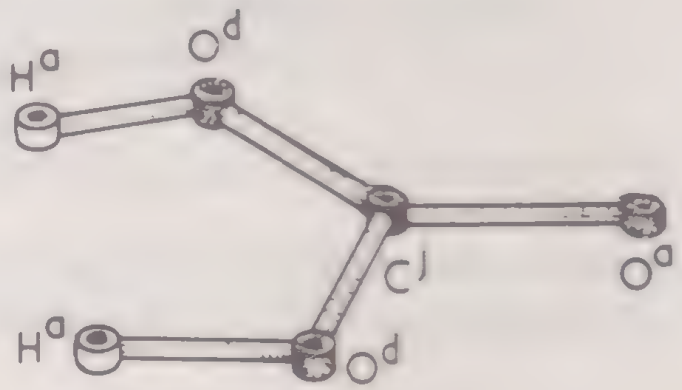


Figure 46 Carbonic acid

Molecules containing 'tetrahedral' nitrogen

The directions of the bonds around a nitrogen atom depend on their number, and upon the number of lone pairs.

Models of amonia, NH_3, and the ammonium ion. NH_4^+, were described on page 5. The principles underlying shapes of molecules were also dealt with on page 5. For further practice, construct a model of methylamine CH_3NH_2 (figure 47).

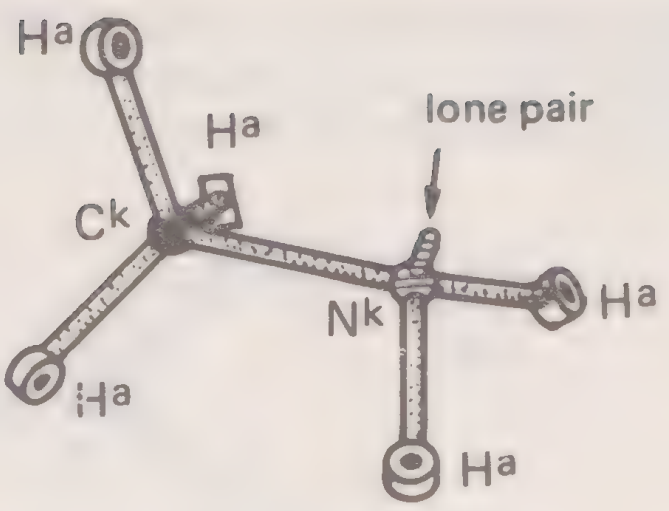


Figure 47 Methylamine

Some oxides of nitrogen

Figure 48 shows the structures of some common oxides of nitrogen, labelled with the code letters of the atomic centres to be used in the construction of the models. It is simpler to omit any attempt at representing double bonds. The bonds marked * may be considered as double bonds. Also, it is simpler to assume that all the bonds are the same length, and to use 2.5 cm (Orbit 5.0 cm) straws throughout, although in fact this is not the case.

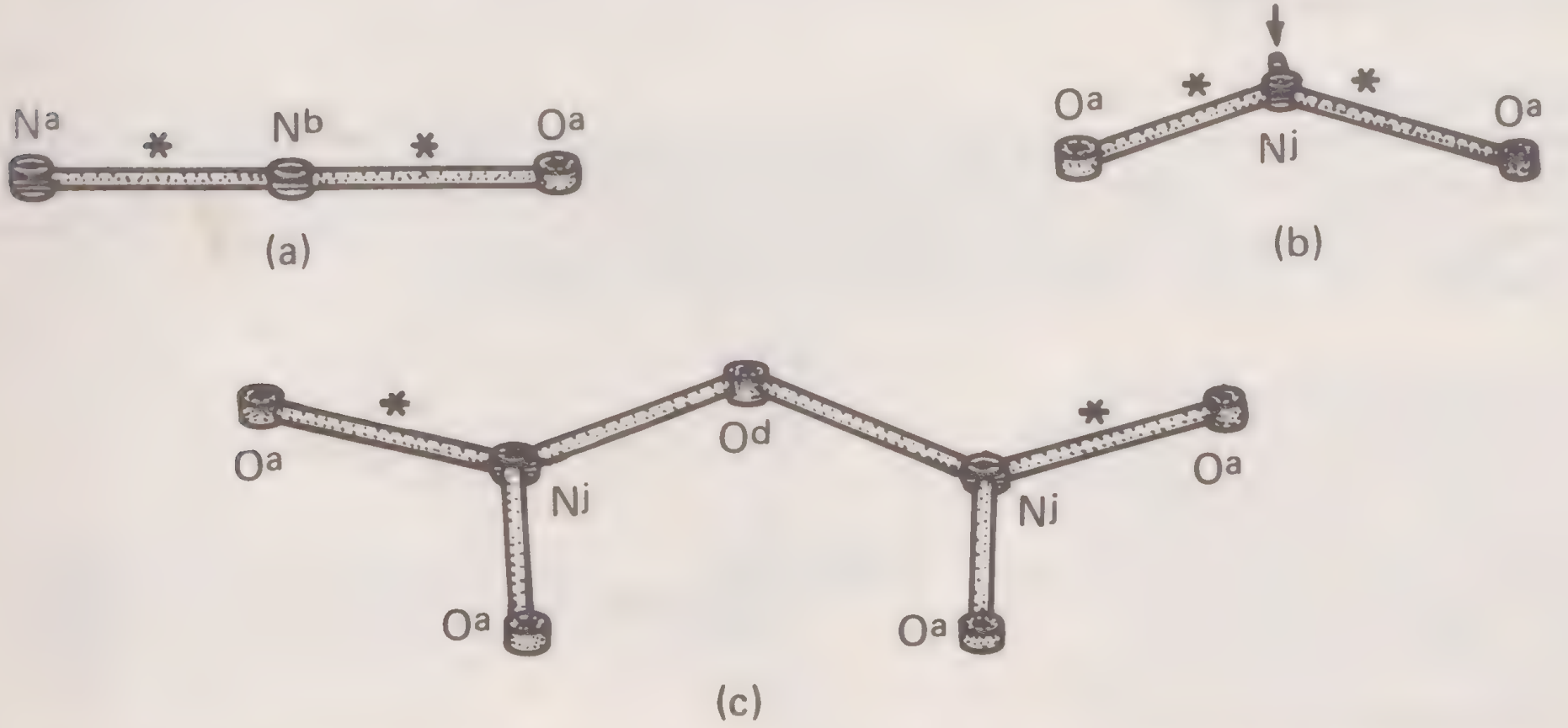


Figure 48 (a) Dinitrogen monoxide, (b) nitrite [nitrate (III)] ion, (c) dinitrogen pentoxide

Nitric acid [nitric (V) acid] HNO_3

Figure 49 shows the structure of nitric acid, together with the code letters of atoms to be used in constructing a model. Also shown is the nitrate ion, NO_3^-.

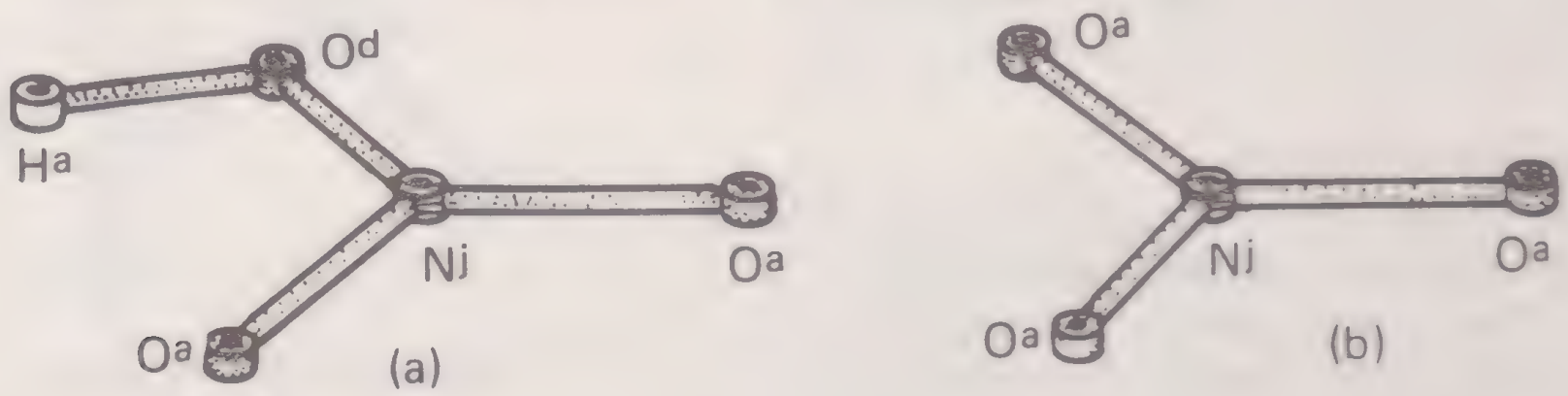


Figure 49 (a) Nitric acid, (b) nitrate ion

Nitrous acid [nitric (III) acid], HNO_2

Nitrous acid contains a lone pair. Its structure may be derived from that of nitric acid simply by removing an oxygen atom together with its bond, and leaving a free prong to denote the lone pair. The nitrite ion [nitrate (III) ion], NO_2^-, may be derived similarly from the nitrate ion, NO_3^-.

Hydrogen cyanide, HCN

Hydrogen cyanide has the structure $H-C\equiv N$. Note that the carbon atom is linear just as in ethyne, $H-C\equiv C-H$ (page 14). Construct a model of hydrogen cyanide, using H^a, C^b, and N^a atoms. The cyanide ion, CN^-, may be represented simply by detaching the hydrogen atom together with its bond. (See also cyano-complexes, page 43).

Organic cyano-compounds, also known as nitriles, may be regarded as derived from hydrogen cyanide by the replacement of the hydrogen atom by an alkyl or other group. For instance, figure 50 illustrates cyanomethane, CH_3CN. Strictly, the $C-N$ bond is a triple bond, $C\equiv N$.

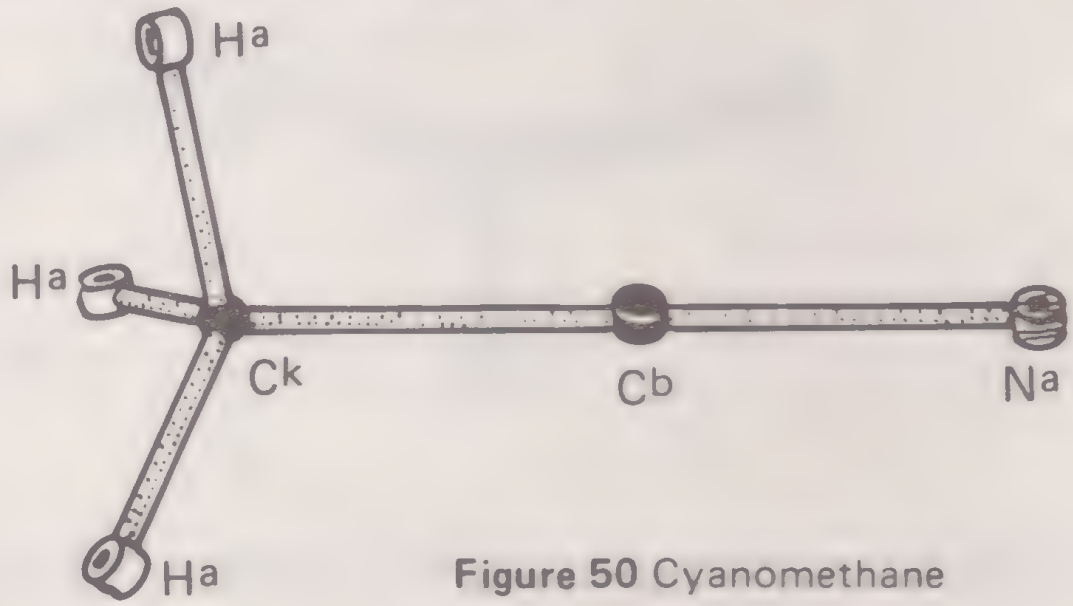


Figure 50 Cyanomethane

White phosphorus, P_4

Figure 51 shows a model of the P_4 molecule. Note that bond distortion occurs and flexible straws have to be used. Use four P^k centres linked by 2.5 cm (Orbit 5.0 cm) flexible straws.

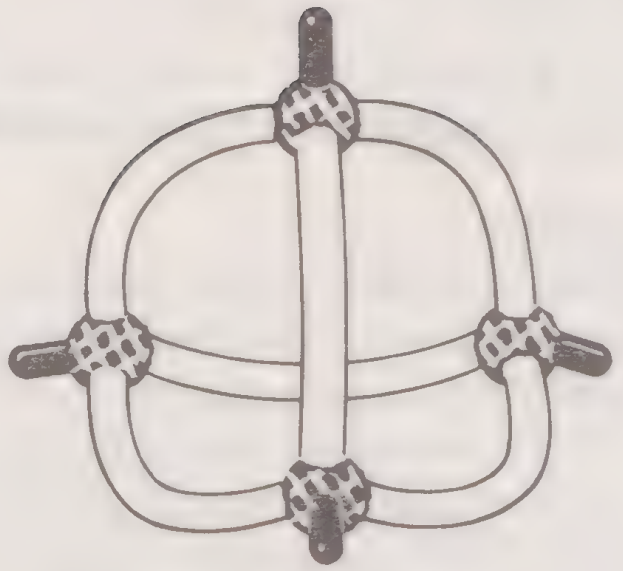


Figure 51 The P_4 molecule

Phosphoric acid, H_3PO_4

Phosphoric acid has a structure in which the central phosphorus atom is tetrahedral. Figure 52 shows its structure, together with the bonds and atomic centres required to construct a model. Note that, for the sake of simplicity, no attempt is made to distinguish between double and single bonds. Use 2.5 cm (Orbit 5.0 cm) green straws for all bonds, except O—H bonds, which require 1.5 cm (Orbit 3.5 cm) straws.

The ions, $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-} may be constructed by removing in turn hydroxyl groups —OH and replacing each with an oxygen centre, O^a.

Phosphorus(V) oxide, P_4O_{10}

This may be constructed as in figure 53, using four tetrahedral phosphorus centres, P^k, six diunivalent oxygen centres, O^d, and four oxygen centres, O^a. The whole structure is based upon the tetrahedron. Phosphorus(V) oxide is the acid anhydride of phosphoric acid. Note that this structure is not unlike that of diamond, in which tetrahedral bonds also determine the shape.

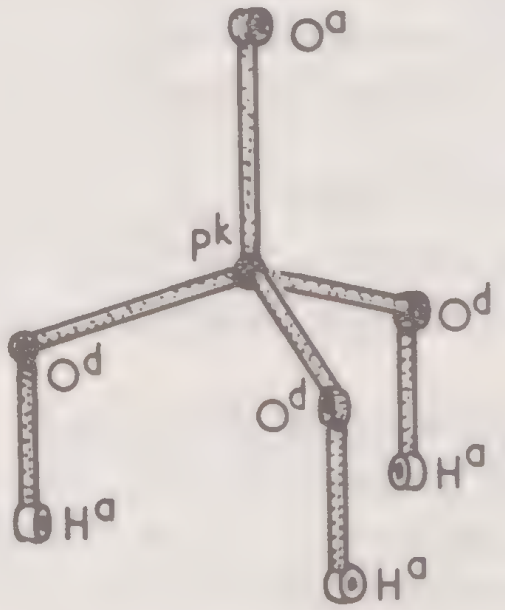


Figure 52 Phosphoric acid

9.2 *Heptaoxodiphosphoric acid has the molecular formula $H_4P_2O_7$. It may be formed by the action of water on phosphorus(V) oxide. Suggest a structure for it, and make a model.*

Phosphorus(III) oxide, P_4O_6

A model of phosphorus(III) oxide can be constructed by removing the four oxygen centres, O^a, from the corners of the phosphorus(V) oxide model constructed as in figure 53.

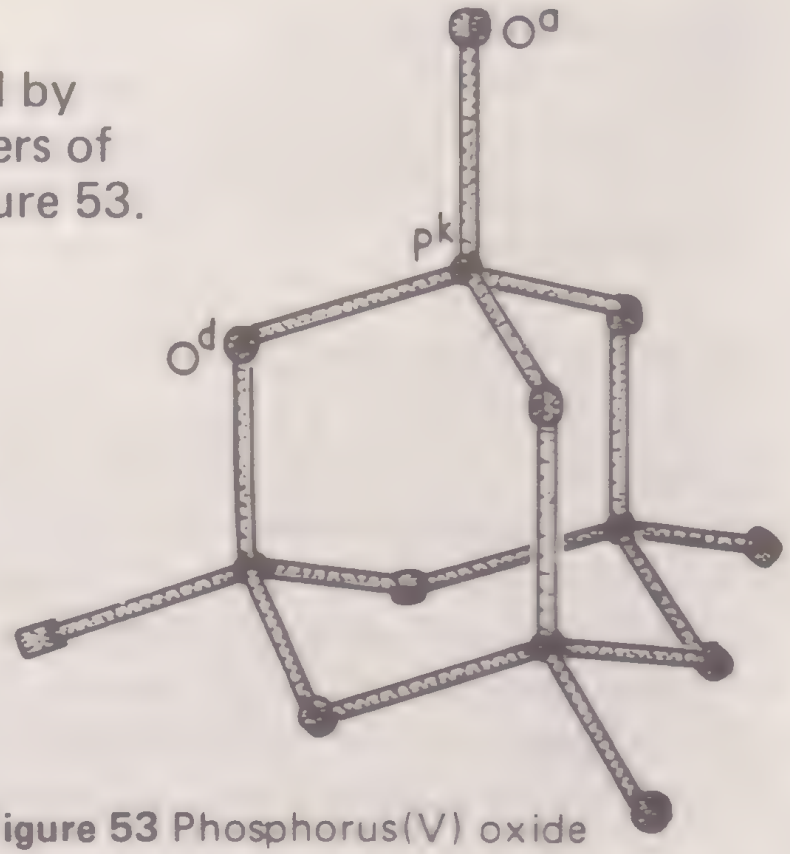


Figure 53 Phosphorus(V) oxide

Sulphur

When a sulphur atom forms two single bonds, two lone pairs are also present. Consequently, the bonds are at an angle of about 100° to one another. The commonest molecular form of sulphur is the ring form, S_8, in which eight atoms with bonds about 100° apart (S^c) unite to form a puckered ring structure, figure 54. Construct a model of this, using 3.5 cm (Orbit 5.0 cm) green straws.

The above ring form is present in orthorhombic and monoclinic sulphur crystals, and persists just above the melting point. Further heating causes the rings to open and link to form polymeric chains. Open an S_8 ring model, and note the zig-zag nature of the chain formed. Chain molecules of this type constitute plastic sulphur.

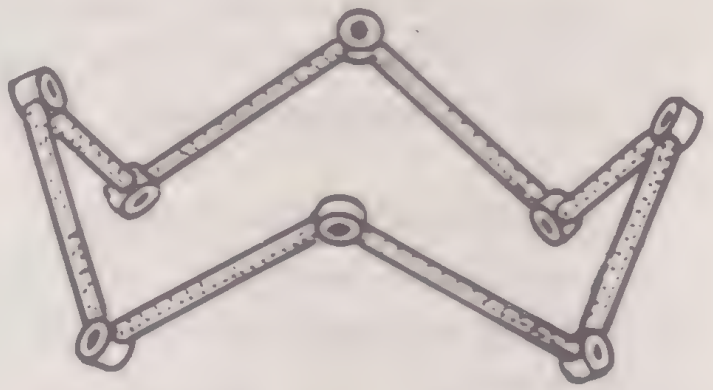


Figure 54 Sulphur ring

Hydrogen sulphide, H_2S

The shape of the hydrogen sulphide molecule is similar to that of the water molecule, but the bond angle is slightly different.

9.3 *Explain why the H_2S molecule is bent rather than linear.*

9.4 *Hydrogen forms polysulphides, H_2S_x, where x = 1 to about 6. Suggest structures for these, and construct models.*

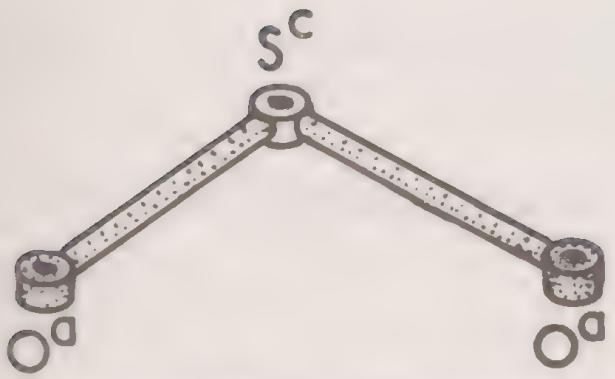


Figure 55 Sulphur dioxide

Sulphur dioxide, SO_2

Sulphur dioxide has a lone pair of electrons on the sulphur atom and is therefore bent. To construct a model, proceed as in figure 55.

Sulphuric acid, H_2SO_4

Sulphuric acid contains a tetrahedral atom at the centre (cf phosphoric acid, page 39). To construct a model of it, proceed as in figure 56. Use 2.5 cm (Orbit 5.0 cm) green straws for S–O bonds, and 1.5 cm (Orbit 3.5 cm) green straws for O–H bonds.

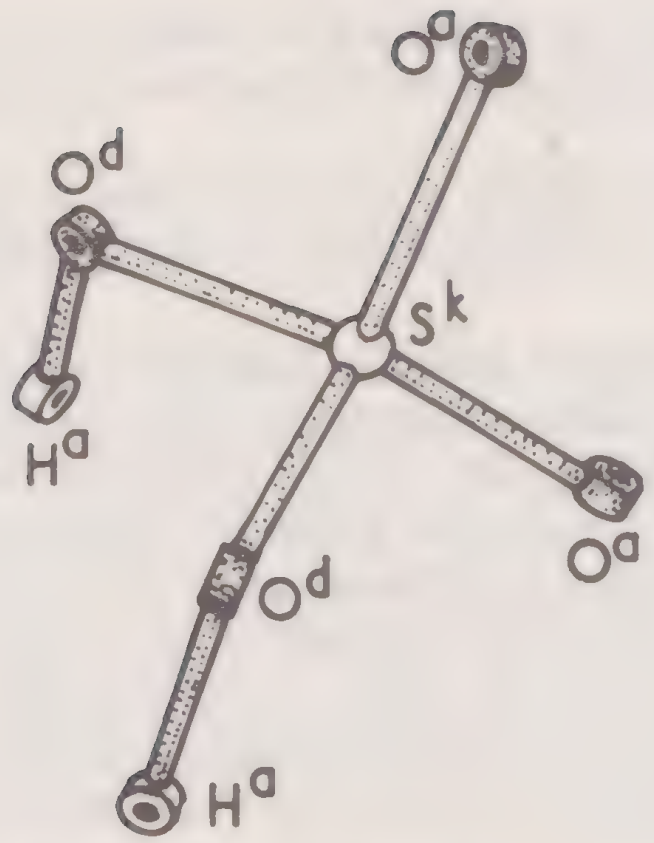


Figure 56 Sulphuric acid

The sulphate ion, SO_4^{2-} may be derived from this structure by removing two hydrogen ions,

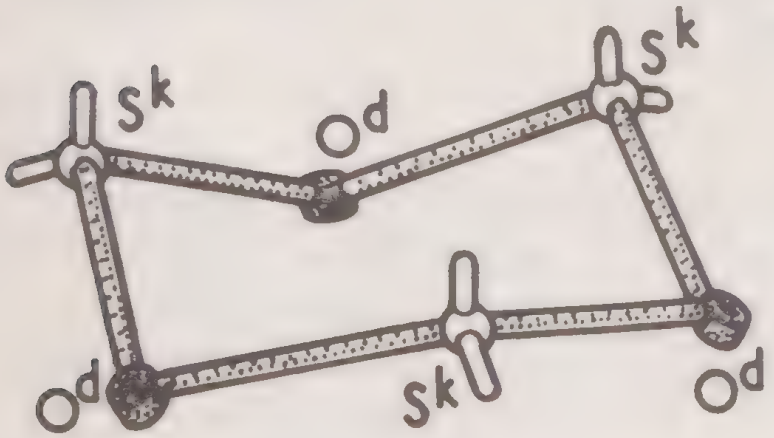


Figure 57

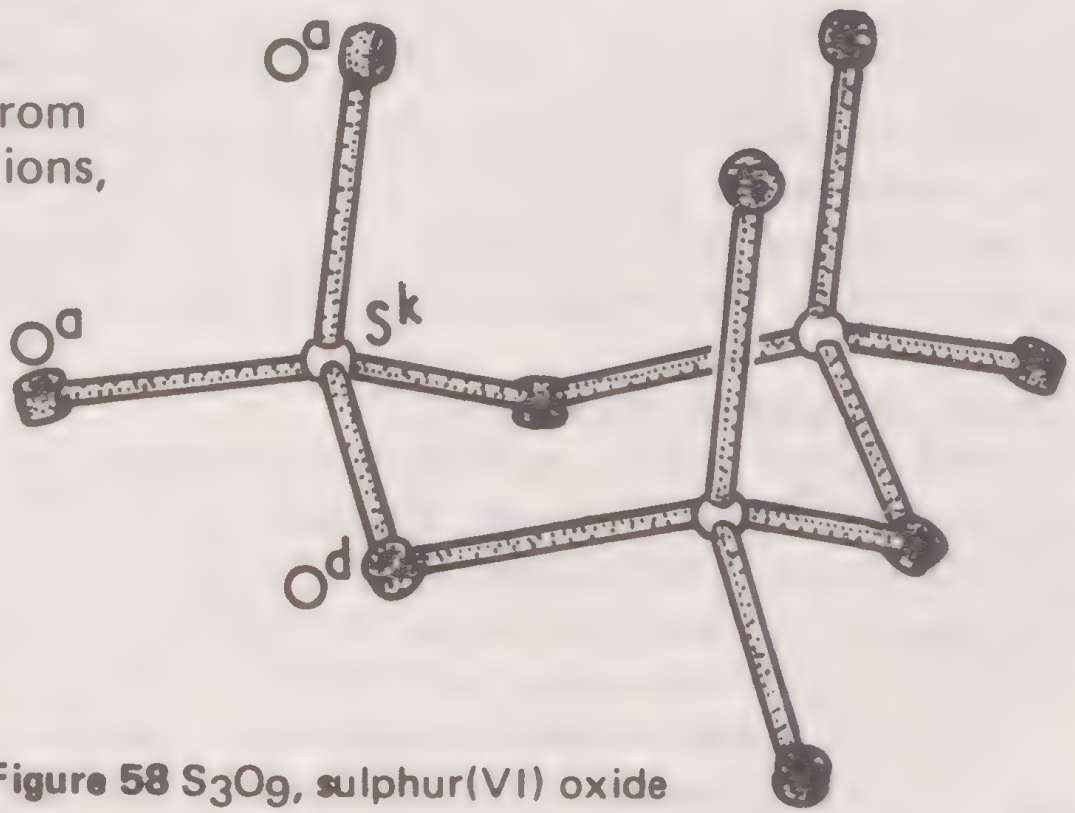


Figure 58 S_3O_9, sulphur(VI) oxide

H^+: to achieve this, detach the two hydroxyl-groups –OH and replace each with an oxygen centre, O^a. Note that the resultant structure has complete tetrahedral symmetry.

9.5 *Name another ion which has the same structure, and also the same electronic configuration, as the sulphate ion* SO_4^{2-}

Sulphur trioxide [sulphur (VI) oxide], SO_3
Strictly speaking the name 'sulphur trioxide' should only be applied to the molecular species SO_3, which only exists at elevated temperatures in the vapour phase. Its shape is based upon a planar triangle with the sulphur atom at the centre. At room temperature 'polymeric' forms exist in the solid state, such as S_3O_9. To construct a model of the latter you will need three sulphur centres S^k, three oxygen centres O^d, and six oxygen centres O^a. Start by constructing a ring using the three S^k and three O^d centres linked by 2.5 cm (Orbit 5.0 cm) straws as in figure 57. Then add the six O^a centres as in figure 58. Note that the resultant structure is in some ways analogous to that of P_4O_{10}.

10 Complex ions

Principles underlying shape
The shape of a complex ion depends upon the number of ligands, and also on factors such as the number of non-bonding electrons present in the uppermost energy levels of the metal atom. Most hexadentate complexes (ie with six points of attachment) are approximately octahedral, and may be represented by using the silver octahedral atom models, M^l. Tetradentate complexes (four points of attachment) are sometimes tetrahedral and sometimes square planar. The latter may be represented in model form by using the octahedral atom models, but omitting to put groups along one axis.

Simple octahedral complexes
Figures 59, 60 and 61 represent respectively the complex ions $Cr(H_2O)_6^{3+}$, $Co(NH_3)_6^{3+}$, and $Fe(CN)_6^{3-}$, to illustrate the general principles. Note that the same silver octahedral atomic centre must be used in every case. In each case, start by constructing models of the ligands, for instance six water molecules using tetrahedral oxygen centres, O^k, or six ammonia molecules using tetrahedral nitrogen centres N^k. Attachment to the central metal atom is then made using straws attached to one of the prongs representing a lone pair on each ligand.

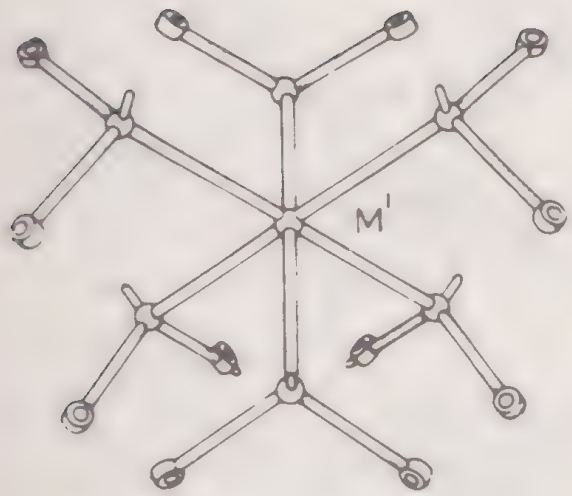


Figure 59
Hexa-aquachromium(III) ion

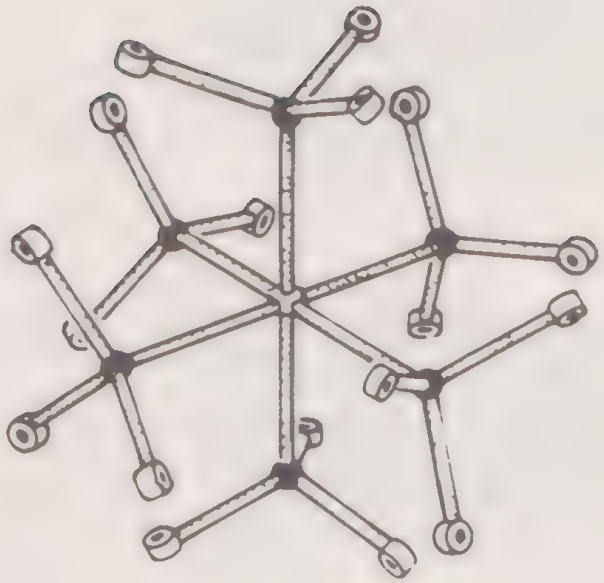


Figure 60
Hexa-amminecobalt(III) ion

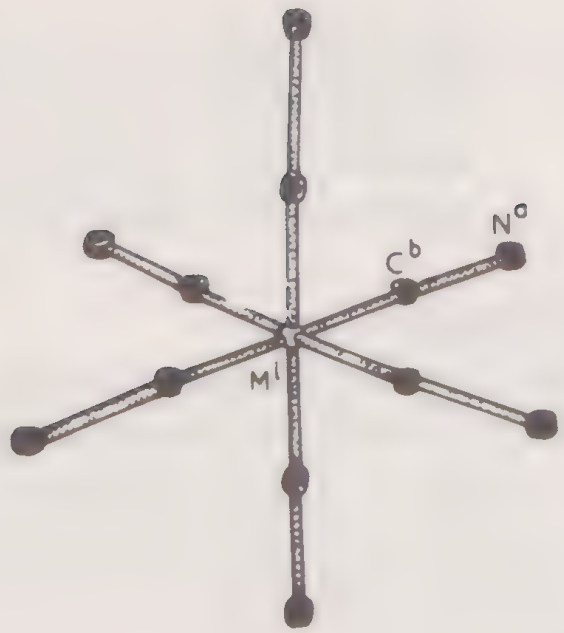


Figure 61
Hexacyanoferrate(III) ion, multiple bonds have been omitted.

Simple tetrahedral complexes

A simple example is tetramminozinc(II). Proceed as in figure 60 above, but use instead a silver tetrahedral atom, M^k and attach only four ammonia molecules. Another interesting example is the uncharged complex, tetracarbonylnickel(0), $Ni(CO)_4$. The ligand here is carbon monoxide, attached to the nickel atom via the lone pair on the carbon atom. Construct four carbonyl ligands using linear carbon atoms C^b linked to oxygen centres O^a. Attach the ligands to a silver tetrahedral centre M^k (figure 62) using 4.0 cm (Orbit 6.5 cm) bonds.

Simple square planar complexes

The ion $Cu(H_2O)_4^{2+}$ is square planar. Remove two ligands from one axis of your model of $Cr(H_2O)_6^{3+}$ The two spare prongs represent the location of one spare non-bonding electron (figure 63).

Figure 62
Tetracarbonylnickel(0) Multiple bonds have been omitted.

10.1 *The complex ion $Pt(H_2O)_2Cl_2^{2+}$ can exist in two isomeric forms. What does this suggest concerning the shape of the ion? What is the relationship between the isomeric forms?*

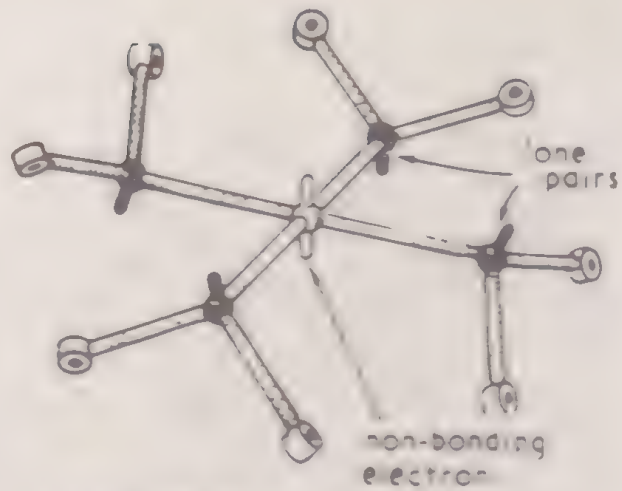


Figure 63
Tetra-aquacopper(II) ion

Bidentate ligands

A ligand which can form two points of attachment with the central atom is said to be bidentate. An example is 1,2-diaminoethane (ethylenediamine), $H_2N.CH_2.CH_2.NH_2$. Construct three models of this. For each you will need two C^k, two N^k and eight H^a.

Take a silver octahedral centre, M^l, and attach the three ligands to it with 4.0 cm (Orbit 6.5 cm) straws. The resultant model could represent for instance $Co(en)_3^{3+}$, where en = 1,2-diaminoethane. (figure 64).

10.2 *Is it possible to construct isomers of $Co(en)_3^{3+}$, assuming the configurations of individual atomic centres to be unchanged?*

Now construct models of $Zn(en)_2^{2+}$ (tetrahedral) and $Cu(en)_2^{2+}$ (square planar).

10.3 *Are either of the above complex ions capable of existing as isomers?*

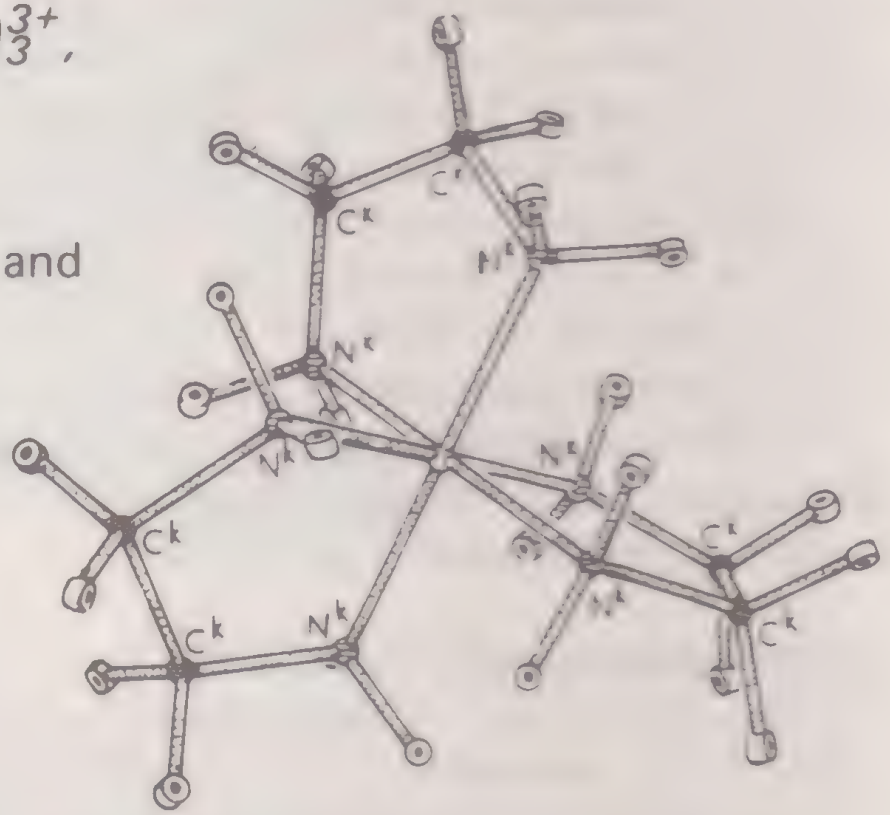


Figure 64
Tris(ethylenediamine)cobalt(III) ion

Notes and answers to questions

1 **Principles of molecular shape**

1.1 The calculated angle is 109° 28′

1.2 No

1.3 Pyramidal

1.4 Tetrahedral: NH_4^+ is isoelectronic with CH_4 and therefore has the same shape

1.5 (a) Bent, for the same reason that H_2O is bent. (b) Pyramidal, since it is isoelectronic with NH_3 (see question 1.3)

1.6 PCl_3 has a pyramidal structure like ammonia and its electronic structure is as shown in diagram 1

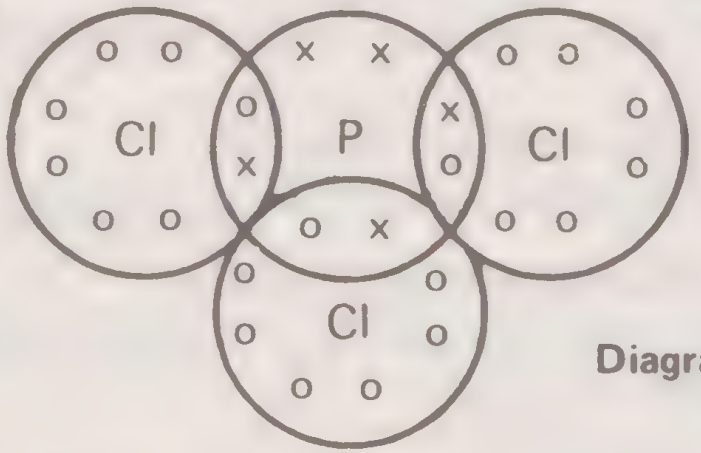
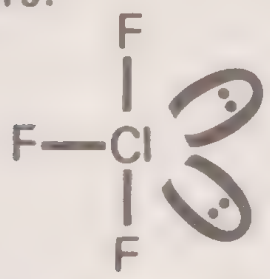
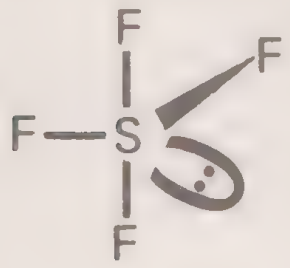


Diagram 1

1.7 The respective electronic structures are as diagrams 2 and 3.
Since both of these molecules have five repelling electron pairs, their shapes will be based on the trigonal bipyramid. ClF_3 is in fact T-shaped with two 'equatorial' lone pairs:



SF_4 has a distorted shape with one equatorial lone pair:



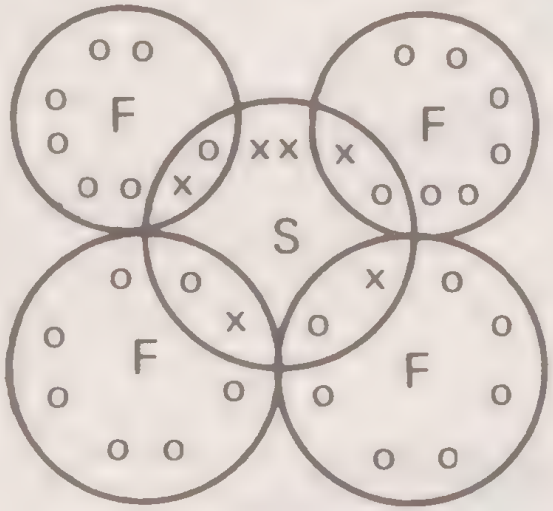


Diagram 2

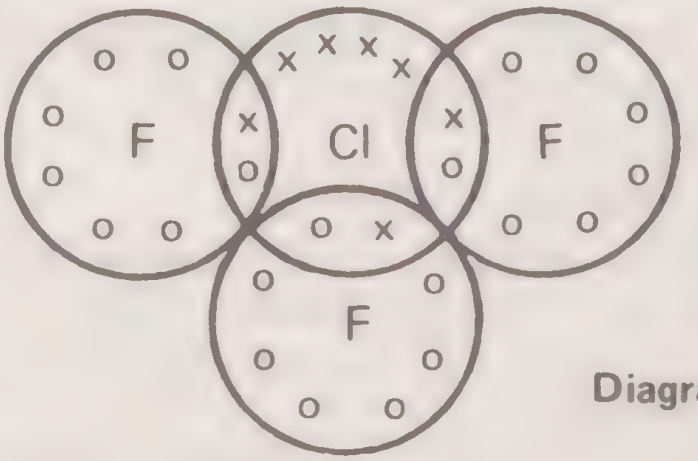


Diagram 3

1.8 The theoretical angle is 90°

1.9 BrF_3 is thought to have the shape of a square pyramid:

2 **Saturated hydrocarbons**

2.1 The theoretical angle is 109° 28′

2.2 Structures (b) and (c) are the same

2.3 Two

2.4 Only one

2.5 Two

2.6 Four (1,1; 2,2; 1,2 and 1,3)

2.7 All these structures are in fact the same

2.8 No

2.9 18, one of which is octane.
(The number of isomers of $C_{40}H_{82}$ is 62 491 178 805 831!)

3 **Unsaturated hydrocarbons**

3.1 The atom centres lie in a plane, though the bent straws project above and below the plane

3.2 Hardly at all

3.3 It is shorter

3.4 Four

3.5 Eight, as in ethane

3.6 No

3.7 Only one

3.8 No

3.9 Yes

4 **Cyclic hydrocarbons**

4.1 109° 28′ − 108° = 1° 28′

4.2 No, because the ring is flat and rigid

4.3 Two (*cis* and *trans* isomers)

4.4 Puckered

4.5 Tetrahedral, ie 109° 28′

4.6 Slightly, ie from one ring conformation to another

4.7 109° 28′. The tetrahedral angle

4.8 It is difficult to join the ends of a long chain to form a ring, since they are initially so far apart

4.9 The bond angle is strained to 90° from the tetrahedral angle

5 Functional groups in organic chemistry

5.1 Because the oxygen atom has two lone pairs

5.2 Two

5.3 Two: $CH_3.O.CH_2.CH_2.CH_3$ and $CH_3.O.CH(CH_3)_2$

5.4 Three: two alcohols and one ether

5.5 14: eight alcohols and six ethers (excluding optical isomers)

6 Benzene and its derivatives

6.1 No

6.2 Three: 1,2; 1,3 and 1,4

6.3 Three, named as for question 6.2

6.4 Tetrahedral. No

6.5 Three. (1,2-dimethylbenzene, 1,3-dimethylbenzene and 1,4-dimethylbenzene)

8 Optical isomerism

8.1 No

8.2 Pair of gloves, shoes, etc

8.3 No

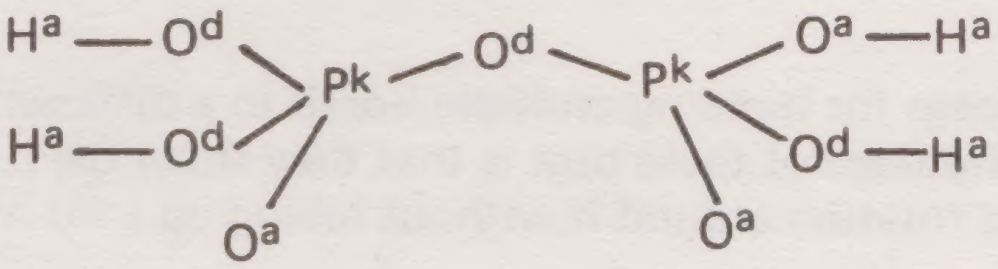
8.4 No, glycollic acid is not asymmetric

8.5 The *cis* acid oxidizes to *meso*-tartaric. The *trans* acid oxidizes to an equimolar mixture of D- and L-tartaric acid (racemic mixture)

9 Simple inorganic molecules

9.1 Linear structure, and similar electronic configuration to CO_2

9.2 Use two P^k centres, five O^d and two O^a and four H^a linked as follows:



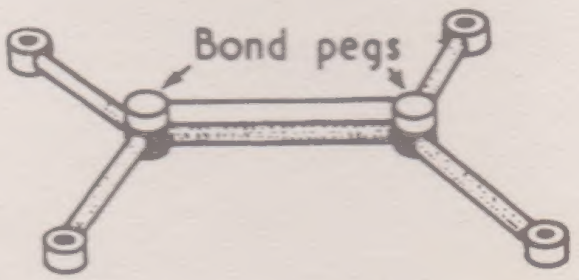
9.3 Because H_2S has two lone pairs on the sulphur atom
9.4 Use a short chain of S^c centres, linked together by 3.5 cm (Orbit 5.0 cm) straws, with an H^a centre at each end of the chain
9.5 PO_4^{3-} and ClO_4^-

10 Complex ions

10.1 It cannot be tetrahedral (it is in fact planar)
10.2 No
10.3 No

Manufacturer's note

"Orbit" sets also include pegs for building multiple bonds in a different form from that shown in the text. The advantage of these pegs is that they show the presence of the multiple bond and restrict rotation around it without taking up a lot of space.



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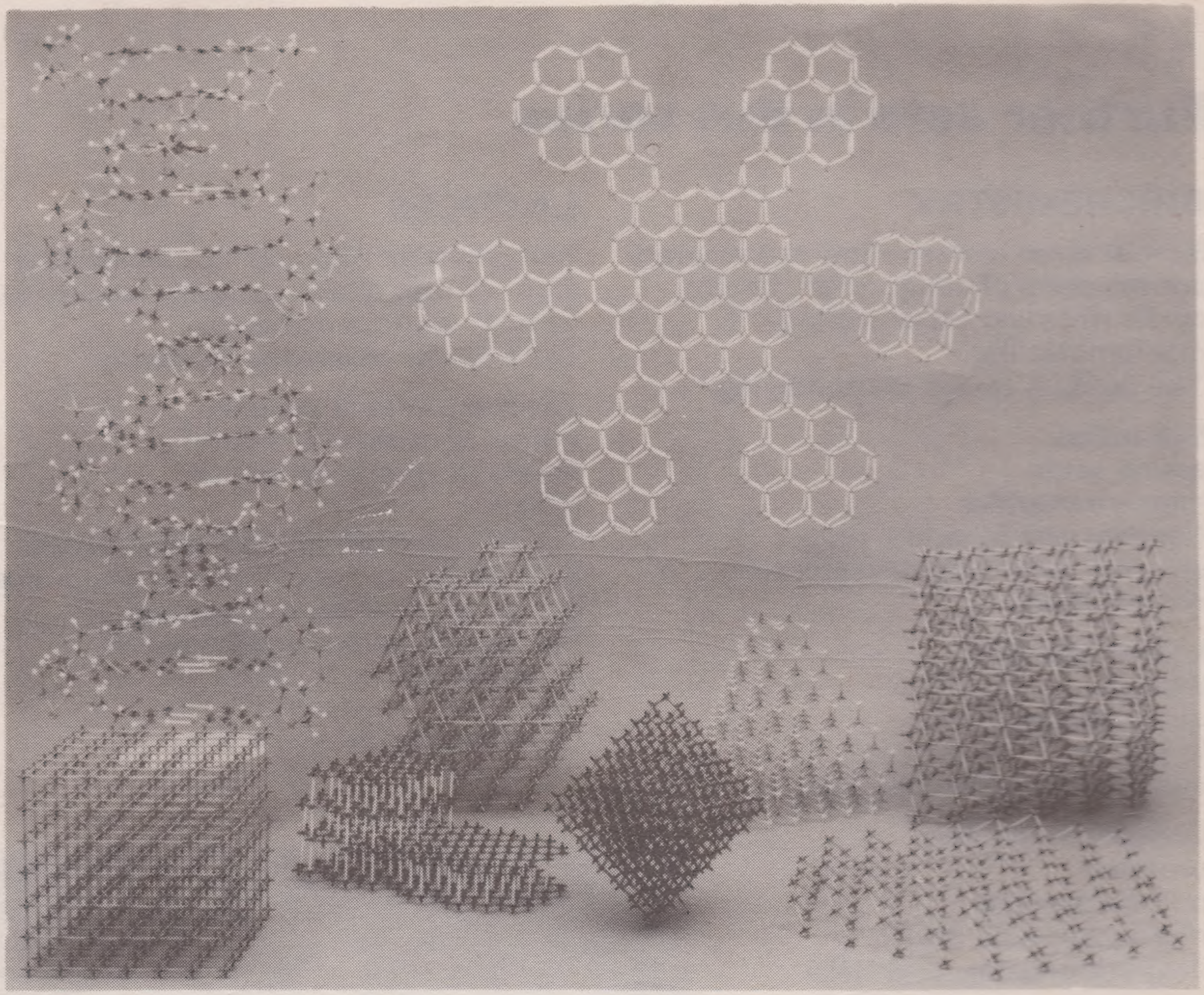

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